THERMOCHEMISTRY AND OXIDATION POTENTIALS OF THE PLATINUM GROUP METALS AND THEIR COMPOUNDS

ROBERT N. GOLDBERG AND LOREN G. HEPLER[1]

Department of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213

Received November 6, 1967

CONTENTS

I. INTRODUCTION

One basic aspect of inorganic and analytical chemistry involves the stabilities of the elements and their compounds. Thermodynamics provides a concise, exact method of organizing and describing these stabilities as well as other equilibrium properties. In this review we are concerned with the chemical thermodynamics, with particular emphasis on aqueous chemistry, of the platinum group elements: ruthenium, osmium, rhodium, iridium, palladium, and platinum.

For each element in the group we give a brief discussion of its descriptive chemistry to define the nature of the species later to be put in order as to their stabilities. Furthermore, a quantitative statement of the equilibrium state of a given reaction mixture cannot violate simple qualitative observations once the kinetic aspects have been accounted for.

We have attempted to be critical in the tabulation of our data and have recalculated many published results. When data from different sources are not in good agreement, we have attempted to justify our choices. Very often in making a choice between conflicting data, we have used our qualitative judgement as to the magnitude of a potential, entropy, etc.

For several compounds and aqueous ions we have combined experimental data from a cited source with our estimate of some thermodynamic property. *Numerical values of our estimates are given in parentheses.*

Uncertainties are particularly difficult to handle. For example, the uncertainty in a given heat of formation determined *via* a Hess' law calculation depends on the cumulative uncertainties of all of the heats of formation used in the calculation. Also, it is often difficult to assign an uncertainty to a given datum, as a reasonable uncertainty is often many times the average deviation of the numbers obtained in the measurements. Furthermore, most work that is generally recognized to be in error is so because of difficulties in the compounds or processes being studied (*i.e.*, unidentified hydrolysis phenomena, nonhomogeneous phases, impurities, etc.) rather than measurement error. Our treatment of uncertainties is simply to tabulate results to a "reasonable" number of figures. In many cases we have indicated that an uncertainty may be larger than usual by placing an approximate sign (~) in front of the cited quantity.

We have been explicit about the sources of data and also our treatment of data from the literature so that interested readers can check the steps leading to the tabulated values of thermodynamic properties and

---

[1] Department of Chemistry, University of Louisville, Louisville, Ky.

form their own opinions about reliability and accuracy. It is also our hope that we have been sufficiently explicit that our tables can be kept up to date as new and hopefully better data appear. In those instances in which we have not been able to read the papers cited, we have also listed the appropriate *Chemical Abstracts* reference or the name of the journal in which the article has been translated.

We have taken most of our auxiliary thermodynamic data from the National Bureau of Standards Technical Note 270-1 (196). Other auxiliary data and their sources are given in Table I.

TABLE I

AUXILIARY THERMODYNAMIC DATA

Substance	$\Delta H_f°$, kcal mole^{-1} (298°K)	Ref
$Cu^{+2}(aq)$	16.4	99a
$CuCl(c)$	−32.2	160
$Co^{+2}(aq)$	−13.9	76
$Ba^{+2}(aq)$	−128.67	160
$BaCl_2(c)$	−205.56	160
$NaCl(c)$	−98.23	160
$KCl(c)$	−104.18	160
$Rb^+(aq)$	−58.9	160
$Cs^+(aq)$	−59.2	160

Although this review is not primarily concerned with high-temperature chemistry, we have made considerable use of data obtained at high temperatures in evaluating the thermodynamic properties of many compounds of the platinum group metals. In the absence of experimental heat content data, we have frequently estimated heat capacity changes ($\Delta C_p°$).

In spite of considerable discussion (3, 51, 121, 154), general agreement is still lacking on "sign conventions" for potentials. Much of the confusion arises because "sign" can be either electrical or algebraic.

Potentials measured in the laboratory are positive or negative in an electrical sense. These electrical cell potentials lead to electrode potentials (based on an arbitrary value for a reference electrode) that are also positive or negative in an electrical sense. The electrical signs of these electrode potentials are independent of how we write the electrode reactions. The standard electrode potential of the Ag|Ag$^+$ electrode at 25° (taking $E° \equiv 0$ for the $H_2|H^+$ electrode) is conveniently represented as ⊕0.8 v, where ⊕ is written to emphasize that the sign is *electrical* and is independent of how we choose to represent the electrode or the reaction that occurs at the electrode.

On the other hand, the potentials that are used in thermodynamic calculations are positive or negative in an *algebraic* sense. We may call these quantities reaction potentials and half-reaction potentials to distinguish them from cell potentials and electrode potentials that have electrical signs. The algebraic signs of these reaction potentials and half-reaction potentials depend on the directions of the reactions or half-reactions under consideration. Thus we write

$$Ag(c) = Ag^+(aq) + e^- \quad E° = -0.8 \text{ v} \quad (\text{Eq } 1)$$

and

$$Ag^+(aq) + e^- = Ag(c) \quad E° = +0.8 \text{ v} \quad (\text{Eq } 2)$$

The potential in Eq 1 may be called an (algebraic) oxidation potential for the Ag|Ag$^+$ half-reaction. *All potentials tabulated in this review are oxidation half-reaction potentials with algebraic signs as in Eq 1.* These tabulated half-reaction potentials are based on the usual references

$$H_2(g) = 2H^+(aq) + 2e^- \quad E° \equiv 0$$

$$H_2(g) + 2OH^-(aq) = 2H_2O(liq) + 2e^- \quad E° = 0.828 \text{ v}$$

The standard states relevant to these standard potentials are also the usual ones (118, 120, 160).

It might be mentioned that our decision to tabulate half-reaction potentials with algebraic signs rather than electrode potentials with electrical signs (+ is not necessarily interchangeable with ⊕) was based on our greater interest in chemical equilibrium and thermodynamics than in electrochemistry. It may be that future tabulations should be made in terms of reduction potentials as in Eq 2 so that + and ⊕ are interchangeable, thus eliminating the need to think about the meaning of sign.

The "sign convention" used here permits straightforward use of the familiar $\Delta G° = -RT \ln K = -nFE°$.

We have reserved the symbols $E°$ and K for potentials and equilibrium constants that have been determined in very dilute solutions or in such ways that activity coefficients could be considered in treating the experimental data. We also calculate $E°$ and K values from $\Delta G°$ data.

For some compounds and ions of interest we lack standard potentials, but we do have data that refer to a particular electrolyte. In reporting such potentials, the superscript° is omitted and the medium is described in parentheses. Most of the data apply at 25°; all are specifically indicated.

Many equilibrium investigations have been carried out in the presence of a large excess of acid, base, or "inert" supporting electrolyte. The results of such investigations lead to equilibrium quotients represented by Q rather than equilibrium constants represented by K. We have used such symbols as $Q_{0.5}$ to indicate that the equilibrium quotient was determined in solutions having ionic strength 0.5.

At the end of the section for each element we have included a potential diagram for that element. Latimer (118) and Jolly (107) have discussed uses of these potential diagrams.

A comprehensive discussion of the analytical chemistry of the platinum group elements may be found in the article by Walsh and Hausman (198). Basolo and Pearson (12) have discussed various aspects of the *trans* effect that are important in relation to the platinum group elements.

II. RUTHENIUM

A. DESCRIPTIVE CHEMISTRY

Although a considerable variety of species that contain ruthenium in oxidation states ranging from −2 to +8 have been reported, we have relevant data for only a few of these states. We begin with a qualitative summary of some of the properties of the various oxidation states, with particular emphasis on species and reactions that are relevant to aqueous solution chemistry.

Metallic ruthenium is unattacked by acids below ~100° and is best brought into solution after fusion with such alkaline oxidizing combinations as $KOH–KClO_3$ or $KOH–KNO_3$. Reaction of the metal with fluorine ordinarily yields RuF_5, although the less stable hexafluoride has also been prepared. The dark brown (β) $RuCl_3$, which is an important starting compound in ruthenium chemistry, is prepared by reaction of Cl_2 (usually mixed with CO) with powdered metal at ~400°. At higher temperatures the black (α) modification of $RuCl_3$ is formed. The dioxide RuO_2 is the only product of reaction of the metal with oxygen at temperatures up to ~700°.

We begin with the +8 oxidation state of ruthenium and proceed toward lower states. The tetroxide RuO_4 is prepared by oxidation of the metal by hot solutions of powerful oxidizing agents such as periodate or permanganate or by oxidation of ruthenate (+6 state) with Cl_2. The volatile yellow tetroxide melts at ~25°, which is also the normal boiling point of the liquid. This poisonous compound is a powerful oxidizing agent and can explode at high temperatures or when mixed with reducing agents. Solution of RuO_4 in aqueous alkali yields oxygen and RuO_4^-, commonly called perruthenate. This ion is a strong oxidizing agent and liberates oxygen from water while it is reduced to ruthenate, RuO_4^{-2}. The tetroxide is only slightly soluble in neutral or acidic solutions and is itself weakly acidic.

The principal compounds of ruthenium in the +6 state are ruthenates containing RuO_4^{-2} ions. The solid ruthenates are prepared by fusion of the metal with appropriate alkaline oxidizing combinations. The orange ruthenate ion is moderately stable in alkaline solution. Alkaline oxidation of most species containing ruthenium in lower oxidation states yields ruthenate. In sulfuric acid there is a green species of Ru(VI) that may be formulated as $[RuO_2(SO_4)_2]^{-2}$.

Various complex fluorides of Ru(V) are known, as well as the pentafluoride already mentioned.

In addition to RuO_2 that is prepared by oxidation of the metal, hydrous oxides of Ru(IV) are known. Reduction of aqueous RuO_4 by hydrogen yields solid $RuO_2 \cdot H_2O$, whereas air oxidation of the hydrous oxide of Ru(III) yields a less well-defined hydrous oxide of Ru(IV). Solid compounds of type $M_2^IRuX_6$ are known for X = F, Cl, and Br, while both $RuCl_6^{-2}$ and $RuBr_6^{-2}$ in aqueous solution have been prepared by treating hydrous RuO_2 with acid.

Both $RuCl_4 \cdot 5H_2O$ and $Ru(OH)Cl_3$ are reduction products of RuO_4 in aqueous HCl. Treatment of various Ru(IV) chloride compounds with ammonia yields "ruthenium red" solutions. These solutions and the solids that can be obtained from them are incompletely characterized but appear to involve trinuclear species containing both Ru(III) and Ru(IV).

Solid RuF_3, $RuCl_3$, $RuBr_3$, and RuI_3 are all known. Commercial "hydrated trichloride" appears to be a complex mixture containing much Ru(IV), but a compound of stoichiometric composition $RuCl_3 \cdot 3H_2O$ has been prepared by evaporation of RuO_4 in aqueous HCl. A black hydrous oxide of Ru(III) is obtained on adding strong base to solutions of $RuCl_3$. The Ru^{+3}(aq) ion is now well established as $Ru(H_2O)_6^{+3}$. In addition, $RuCl(H_2O)_5^{+2}$ and both *cis*- and *trans*-$RuCl_2(H_2O)_4^+$ have been characterized. The ion $RuCl_5(H_2O)^{-2}$ is apparently present in concentrated HCl. A considerable number of ammine complexes of Ru(III) are known. The complex fluoride K_3RuF_6 that is prepared by fusion of $RuCl_3$ with KHF_2 dissolves in dilute acid to yield solutions in which RuF_6^{-3} ions appear to be the principal species.

Only a few simple compounds of Ru(II) are known, among which is $RuCl_2$. A considerable number of complexes of Ru(II) have been obtained by reduction of solutions of Ru(III) or Ru(IV) that contain appropriate ligands. Reduction of ruthenium chloride solutions yields soluble blue chloro complexes of Ru(II) that react with water. The $Ru(H_2O)^{+2}$ ion is obtained when tetrafluoroborate or *p*-toluenesulfonate is the anion. Both the $Ru(dipy)_3^{+2}$ and $Ru(CN)_6^{-4}$ complexes are quite stable.

Ruthenium pentacarbonyl, $Ru(CO)_5$, and several related compounds containing ruthenium in the zero oxidation state have been prepared and investigated. Among the derivatives are species that appear to contain ruthenium in the −2 oxidation state. We have no data relevant to this article for any of these compounds.

B. THERMOCHEMISTRY

We now turn to detailed consideration of thermodynamic properties of ruthenium and its compounds, with emphasis on work relevant to aqueous solutions. For Ru(c) and Ru(g) we adopt entropies tabulated by Kelley and King (112). Three recent investigations

(36, 145, 146) lead to ΔH°_{298} for sublimation of ruthenium. We adopt ΔH_f° = 155 kcal mole^{-1} for Ru(g) from two of these (36, 145) and calculate ΔG_f° by combination with the entropies.

For RuO_2(c) we have $\Delta H_f^\circ = -73$ kcal mole^{-1} from a calorimetric investigation (177). Two investigations (17, 165) of vapor pressures of oxygen lead to slightly less exothermic values for ΔH_f° of RuO_2(c). We adopt $\Delta H_f^\circ = -73$ kcal mole^{-1} for RuO_2(c) and combine with S° = 14 cal deg^{-1} mole^{-1} (17, 165) to obtained $\Delta G_f^\circ = -61$ kcal mole^{-1}.

Two calculations (142, 167) are in good agreement with S°_{298} = 69.4 cal deg^{-1} mole^{-1} for RuO_4(g). Calorimetric measurements (135) lead to $\Delta H_f^\circ = -57$ kcal mole^{-1} for RuO_4(c) and $\Delta H_f^\circ = -55$ kcal mole^{-1} for RuO_4(liq). Combination of these values with vapor pressure data (133) leads to the other thermodynamic functions for RuO_4 listed in Table II. Appearance potentials (56) for Ru^+(g), RuO^+(g), RuO_2^+(g), RuO_3^+(g), and RuO_4^+(g) from RuO_4(g) permit calculation of ΔH_f° values for these gaseous ions.

Heat capacity and vapor pressure data have been combined (205) to yield the values cited in Table II for RuS_2(c).

TABLE II

THERMODYNAMIC DATA FOR RUTHENIUM AT 298°K[a]

Substance	ΔH_f°. kcal mole^{-1}	ΔG_f°. kcal mole^{-1}	S°. cal deg^{-1} mole^{-1}
Ru(c)	0	0	6.82[112]
Ru(g)	155[36,145]	144	44.55[112]
RuO_2(c)	−73[177]	−61	14[17,165]
RuO_2(c, hyd)		−51[45,46]	
RuO_4(c)	−57[135]	−36[133]	35[133]
RuO_4(liq)	−55[135]	−36[138]	44[133]
RuO_4(g)	−44[183]	−33[133]	69.4[142,167]
RuO_4(aq)	∼−57[134,158]	−35[134,158]	∼31[134,158]
H_2RuO_5(aq)		−92[134,158]	
$HRuO_5^-$(aq)		−76[118,124]	
$HRuO_4^+$(aq)		−35[124]	
RuO_4^-(aq)		−58[187]	
RuO_4^{-2}(aq)		−72[45,123,187]	
RuS_2(c)	∼−53[109,205]	∼−50[109,205]	∼10[109,205]
RuF_5(c)	−213.4[151]		
RuF_6(g)			∼82[132]
$RuCl_3$(c)	∼−61[13]	∼−44[18]	∼30[13]
$RuBr_3$(c)	∼−33[172]		
RuI_3(c)	−16[173]		

[a] Superscript numbers are references.

For RuF_5(c) we have ΔH_f° from direct calorimetric measurements (151). Vapor pressure data have been reported (202). The approximate S°_{298} for RuF_6(g) was calculated (132) from molecular constants.

Dissociation pressure measurements on $RuCl_3$(c) at high temperatures are in poor agreement with one another. Recent investigations by Shchukarev, Kolbin, and Ryabov (171) lead to $\Delta H_f^\circ \cong -49$ kcal mole^{-1} for $RuCl_3$(c), whereas the data of Bell, Garrison, and Merten (13) lead to $\Delta H_f^\circ \cong -61$ kcal mole^{-1}. We adopt the latter value because it relates to the most "reasonable" entropy for $RuCl_3$(c) and because it appears to be in agreement with the least uncertain of the older work (157). Other high-temperature measurements (14, 113) lead to inconsistent values for $RuCl_3$(g) and $RuCl_4$(g).

Shchukarev, Kolbin, and Ryabov (172, 173) have also studied the high-temperature decomposition of $RuBr_3$(c) and RuI_3(c). We tabulate only the heats of formation, as their results lead to $RuBr_3$(c) having a higher entropy than RuI_3(c). The heat of formation of RuI_3(c) as determined (173) by conversion of RuI_3(c) to RuO_2(c) in a bomb calorimeter is in good agreement with the value obtained *via* the high-temperature decomposition experiments. It should be noted that we take Br_2(liq) and I_2(c) as reference states.

Vapor pressures (134) of RuO_4 over its aqueous solutions lead to $\Delta G_f^\circ = -35$ kcal mole^{-1} for RuO_4(aq). The solubility (158) of RuO_4(c) at 25° leads to the same value. Data for other temperatures (134, 158) are not completely self-consistent but lead to the approximate values of ΔH_f° and $\bar{S}_2^\circ$ listed in Table II for RuO_4(aq).

Latimer (118) has quoted Silverman and Levy as reporting $K = 1.3 \times 10^{-12}$ for the acid ionization constant of "perperruthenic" acid represented by

$$H_2RuO_5(aq) = H^+(aq) + HRuO_5^-(aq)$$

Martin (124) has reported $K = 6.8 \times 10^{-12}$ at 20° for this same same ionization. Both values are reasonably consistent with the free energies given in Table II for aqueous H_2RuO_5 [$\Delta G^\circ = 0$ for $RuO_4(aq) + H_2O(liq) = H_2RuO_5(aq)$] and $HRuO_5^-$. Martin (124) has also reported the following.

$$H_2RuO_5(aq) = OH^-(aq) + HRuO_4^+(aq) \qquad K(20^\circ) = 5.7 \times 10^{-15}$$

As a result of investigations by Silverman and Levy (187) and Connick and Hurley (45, 46), we are able to give a consistent set of free energies for hydrous RuO_2, RuO_4^{-2}(aq), and RuO_4^-(aq). Polarographic (187) and equilibrium measurements (123) in alkaline solutions have led to the following potentials.

$$RuO_4^-(aq) = RuO_4(aq) + e^- \qquad E^\circ = -1.00 \text{ v}$$

$$RuO_4^{-2}(aq) = RuO_4^-(aq) + e^- \qquad E^\circ = -0.59 \text{ v}$$

Reversible cell measurements (45) have led to the same potential for the $RuO_4^{-2}|RuO_4^-$ half-reaction. Equilibrium measurements (45, 46) yield equilibrium constants for disproportionation of RuO_4^{-2}(aq) in alkaline solution and for disproportionation of RuO_4^-(aq) in acidic solution as follows.

$$3RuO_4^{-2}(aq) + (2 + x)H_2O(liq) = 2\,RuO_4^-(aq) + RuO_2 \cdot xH_2O + 4OH^-(aq) \qquad K = 6 \times 10^{-9}$$

$$4RuO_4^-(aq) + 4H^+(aq) = 3RuO_4(aq) + RuO_2 \cdot xH_2O + (2 - x)H_2O(liq) \qquad K = 2.5 \times 10^{27}$$

For our thermodynamic calculations we take $x = 0$ and represent the hydrous dioxide by RuO_2(c, hyd). The resulting free energies of formation, which are listed in Table II, permit calculation of the additional potentials

$$RuO_2(c, hyd) + 4OH^-(aq) = RuO_4^{-2}(aq) + 2H_2O(liq) + 2e^- \quad E^\circ = -0.35 \text{ v}$$

$$RuO_2(c, hyd) + 4OH^-(aq) = RuO_4^-(aq) + 2H_2O(liq) + 3e^- \quad E^\circ = -0.43 \text{ v}$$

$$RuO_2(c, hyd) + 2H_2O(liq) = RuO_4(aq) + 4H^+(aq) + 4e^- \quad E^\circ = -1.40 \text{ v}$$

$$RuO_2(c, hyd) + 5OH^-(aq) = HRuO_5^-(aq) + 2H_2O(liq) + 4e^- \quad E^\circ = -0.54 \text{ v}$$

$$Ru(c) + 2H_2O(liq) = RuO_2(c, hyd) + 4H^+(aq) + 4e^- \quad E^\circ = -0.68 \text{ v}$$

$$Ru(c) + 4H_2O(liq) = RuO_4(aq) + 8H^+(aq) + 8e^- \quad E^\circ = -1.04 \text{ v}$$

The ΔG_f° for RuO_2(c, hyd) differs by 10 kcal mole^{-1} from the ΔG_f° cited for RuO_2(c). This difference seems unusually large, but we have no specific reason to question any of the relevant data.

Hydrous RuO_2 is only slightly soluble in dilute perchloric acid. Solubility data (18) show that the average charge on Ru(IV) species in these solutions is +2. Other experiments showed that there are polymeric Ru(IV) species in acidic solution and also led to identification of ruthenyl ion, RuO^{+2}(aq), as an important species. An approximate free energy that we calculate from the solubility data leads to a potential of ∼−1.4 v for the Ru(IV)|RuO_4 couple in acidic solution. This value is supported by previously reported (201) approximate potentials of −1.40 (1 *M* $HClO_4$), −1.43 (6 *M* $HClO_4$), and −1.51 (9 *M* $HClO_4$) for the Ru(IV)|RuO_4 couple. It should be noted, however, that Donnan membrane measurements (197) indicate a charge of +4 for ions of Ru(IV) in aqueous perchloric acid.

We now turn to some potential data that cannot be directly related to the free energies so far cited. Buckley and Mercer (31) have determined

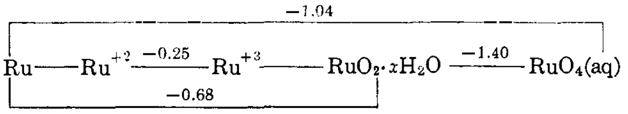
$$Ru^{+2}(aq) = Ru^{+3}(aq) + e^- \quad E^\circ = -0.249 \text{ v}$$

in solutions derived from *p*-toluenesulfonic acid. Measurements at three temperatures also led them to ΔH° and ΔS° values that permit us to calculate $\bar{S}_2^\circ(Ru^{+3}) - \bar{S}_2^\circ(Ru^{+2}) = +37$ cal deg^{-1} mole^{-1}. This entropy difference is negative for other pairs of +3/+2 ions, and it is difficult to account for the above large positive value.

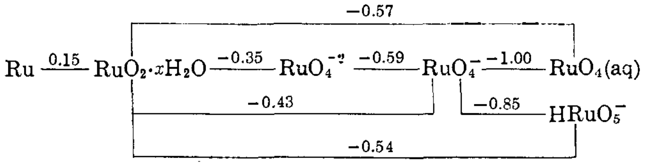
Since neither the Ru|Ru^{+2} nor the Ru^{+3}|RuO_2 potential has been measured, we are unable to use the Ru^{2+}|Ru^{+3} potential in calculating ΔG_f° values. Latimer (118) estimated $E^\circ = (-0.45)$ v for the Ru|Ru^{+2} couple, which is combined with the reported Ru^{+2}|Ru^{+3} potential to indicate that Ru^{+2} is unstable with respect to disproportionation. If we accept this estimate, it permits us to calculate the potential of the Ru^{+3}|RuO_2(c, hyd) couple to be (−1.6) v. It should be noted, however, that Buckley and Mercer (31) report that Ru^{+2} is stable with respect to disproportionation. On this basis, it appears that a better estimate for the Ru|Ru^{+2} potential would be $E^\circ = (-0.2)$ v, which leads to $E^\circ = (-2.1)$ v for the Ru^{+3}|RuO_2(c, hyd) couple. This latter value appears to be far too negative. These difficulties can be lessened, but not eliminated, by taking the ΔG_f° for RuO_2(c, hyd) closer to that for RuO_2(c). In the absence of further experimental data to resolve these uncertainties and discrepancies, we omit some ΔG_f° values from Table II and also leave blank spaces in the potential diagram for acidic solutions.

SCHEME I

ACIDIC SOLUTION



BASIC SOLUTION



We have data for several other couples as follows. Both equilibrium and cell measurements (67) lead to

$$Ru(NH_3)_6^{+2}(aq) = Ru(NH_3)_6^{+3}(aq) + e^- \quad E^\circ = -0.21 \text{ v}$$

An approximate potential for the $Ru(NH_3)_5^{+2}$|$Ru(NH_3)_5^{+3}$ couple was also reported (67). DeFord and Davidson (52) reported

$$Ru(CN)_6^{-4}(aq) = Ru(CN)_6^{-3}(aq) + e^- \quad E^\circ = -0.86 \text{ v}$$

and gave information about slightly soluble compounds of these ions with a number of monatomic metal ions.

Equilibrium constants for NO complexes of Ru(III) have been reported (126).

Several investigators have reported data relevant to aqueous species of Ru(IV). Grube and Fromm (94) gave E(0.5 *M* HCl) = −0.9 v for the Ru(III)|Ru(IV) couple. This value is in reasonable agreement with that reported by Backhouse and Dwyer (9), but differs considerably from the value reported by Atwood and De Vries (6) for $HClO_4$ solutions. These latter investigators (6, 10) have also reported potentials for Ru(II) and Ru(III), and some evidence for a mixed species containing both Ru(III) and Ru(IV) has been presented (6). Buckley and Mercer (31) also report some approximate potentials determined polarographically for complex chlorides of Ru(II)|Ru(III).

We also call attention to a recent investigation (28) of the system

$$Ru(NH_3)_5(H_2O)^{+3}(aq) + Cl^-(aq) = Ru(NH_3)_5Cl^{+2}(aq)$$

Measurements made from 35 to 90° lead to $K_{298} \cong 110$, $\Delta H \cong 1.7$ kcal mole^{-1}, and $\Delta S \cong 15$ cal deg^{-1} mole^{-1}.

Many of the potentials discussed above and the related stabilities of various oxidation states can be summarized by the potential diagrams in Scheme I.

III. OSMIUM

A. DESCRIPTIVE CHEMISTRY

The chemistry of osmium involves a considerable variety of species that contain osmium in all oxidation states from 0 to +8. We begin with a qualitative summary of some of the properties of the various oxidation states, with particular emphasis on species and reactions that are relevant to aqueous solution chemistry.

Metallic osmium is unattacked by acids below ~100°, but reaction at higher temperatures with oxidizing acids can yield OsO_4, which is also formed by combustion of the metal in air at temperatures above ~200°. Although the metal resists fusion with such acidic substances as $KHSO_4$, it is readily brought into aqueous solution after fusion with such alkaline oxidizing combinations as $KOH–KClO_3$. Reaction of the metal with fluorine ordinarily yields OsF_6, and it has been shown that OsF_8 is not formed, contrary to earlier reports. There is a recent report (75) of formation of OsF_7, which decomposes to OsF_6 and F_2. Chlorine oxidizes the metal to $OsCl_3$ or $OsCl_4$, depending on conditions. On heating, the metal reacts with S, Se, or Te to form OsS_2, $OsSe_2$, and $OsTe_2$.

The tetroxide, OsO_4, is the most important compound containing osmium in the +8 oxidation state. This volatile compound is very poisonous. It is quite soluble in several organic solvents and is used in organic chemistry as an oxidizing agent for the specific preparation of *cis*-diols. The tetroxide is moderately soluble in water and acidic solutions and is used as a catalyst for several oxidations relevant to quantitative analysis, such as the oxidation of arsenious acid by ceric solution. Although the octafluoride has not been made and is probably unstable, the oxyfluoride of formula OsO_3F_2 is known. Salts containing $OsO_3F_3^-$ and $OsO_4F_2^{-2}$ ions have been prepared. The so-called "perosmate" ion that may be represented by $OsO_4(OH)_2^{-2}$(aq) is known in alkaline solution. Reaction of the latter with ammonia yields the osmiamate ion of formula OsO_3N^- [containing Os(VIII) and an $Os{\equiv}N$ bond] and thence several salts.

The only compounds containing Os(VII) are $OsOF_5$, salts of OsO_6^{-5} and OsO_5^{-3}, and the previously mentioned OsF_7.

Gaseous OsO_3 has been identified, but neither the corresponding solid nor a hydroxide containing Os(VI) has been established. Alkaline oxidation of metallic osmium commonly yields such osmates as K_2OsO_4. The +6 oxidation state is also often obtained by reduction of alkaline solutions of OsO_4 ("perosmate") with alcohol. There is evidence that the aqueous osmate anion is most realistically represented by $[OsO_2(OH)_4]^{-2}$(aq) rather than by OsO_4^{-2}(aq). The osmate ion is pink in aqueous solution but is blue in methanol. Both $OsOF_4$ and $OsOCl_4$ are known and Cs_2OsOCl_6 has been reported. Several "osmyl" and "oxy-osmyl" salts containing $OsO_2X_4^{-2}$ and $[OsO_2(OH)_2X_2]^{-2}$ ions have been identified.

The pentafluoride has been obtained from decomposition of OsF_6, and the mixed halide $OsIF_4$ has also been reported. Salts containing the OsF_6^- ion have been prepared.

The dioxide of Os(IV) is prepared by heating the metal with either NO or OsO_4. The dihydrate, $OsO_2 \cdot 2H_2O$, is obtained by reduction of OsO_4 in alkaline solution or by adding base to an acidic solution containing OsX_6^{-2} ions. Reduction of OsO_4 with aqueous alcohol in presence of excess KCl yields K_2OsCl_6, which is often used as a starting material for subsequent work with osmium. Stable OsX_6^{-2} ions are known for all the halides. A few mixed halide species have been reported to exist in solution. Tetrahalides are known for fluorine, chlorine, and bromine, but not for iodine.

Early reports of the oxide of Os(III) are questionable. Well-defined OsX_3 compounds are known for Cl, Br, and I. The trichloride, which may be prepared by heating $(NH_4)_2OsCl_6$ in Cl_2, sublimes at about 350° and disproportionates to $OsCl_2$ and $OsCl_4$ at higher temperatures. The trichloride is appreciably soluble in both water and alcohol. Salts of OsX_6^{-3} are known but are unstable because of easy oxidation. Complex species of Os(III) include $Os(NH_3)_6^{+3}$, $Os(en)_3^{+3}$, and $Os(dipy)_3^{+3}$.

The most recent report known to us of an oxide of osmium in the +2 state was made in 1863. The inert $OsCl_2$ and the iodide OsI_2 are both well-established compounds. Several carbonyl halides of +2 osmium have been reported, and a number of nitrosyl and sulfite complexes are known.

For +1 osmium we have the iodide OsI and carbonyl bromides and iodides of formula $[Os(CO)_4X]_2$.

The only known compounds of osmium in the zero oxidation state are the carbonyls with formulas $Os(CO)_5$ and $Os_3(CO)_{12}$.

Further descriptive chemistry of osmium may be found in the review by Griffith (79).

B. THERMOCHEMISTRY

We now turn to detailed consideration of thermodynamics of osmium and its compounds, beginning with the element. We take entropies of Os(c) and Os(g) from Kelley and King (112). Two recent investigations (36, 145) lead to $\Delta H_f° = 189.0 \pm 1.4$ and 187.4 ± 0.9 kcal mole^{-1} for Os(g). We adopt $\Delta H_f° = 188$ kcal mole^{-1} and combine with the entropies to obtain $\Delta G_f°$. For $Os^+(g)$ we obtain $\Delta H_f° = 390$ kcal mole^{-1} by adjusting the value (based on arc spectral data) cited in NBS Circular 500 (160) for the revised $\Delta H_f°$ of Os(g). A recent appearance potential measurement (56) on $OsO_4(g)$ leads to $\Delta H_f° = 419 \pm 12$ kcal mole^{-1} for $Os^+(g)$. The discrepancy is unexplained. Appearance potential data are also available (56) for other gaseous ions of osmium.

For $OsO_4(g)$ we have $S°_{298} = 70.1$ cal deg^{-1} mole^{-1} from Kelley and King (112) and 70.3 cal deg^{-1} mole^{-1} from more recent calculations (167). We adopt the latter value. From the data of von Wartenburg (195) we calculate $\Delta H_f° = -94$ (± 2?) kcal mole^{-1} for OsO_4(c, yellow). We calculate $S°_{298} = 35$ cal deg^{-1} mole^{-1} for OsO_4 (c, yellow) from the entropy of vaporization taken from Kelley's review (110) of vapor pressure data. These same data also lead to $\Delta G_f°$ and $\Delta H_f°$ for $OsO_4(g)$ after $\Delta G_f°$ for OsO_4(c, yellow) has been calculated from its $\Delta H_f°$ and $S°$. Kelley's (110) summary of data for vaporization of OsO_4(c, white) also permits calculation of $\Delta H_f°$, $\Delta G_f°$, and $S°_{298}$ for this substance. The yellow form is slightly ($\sim$0.3 kcal mole^{-1}) more stable than the white form at 298°K.

The solubility of $OsO_4(c)$ in water was determined by Anderson and Yost (2) (note that the solubility cited in their Table I is apparently correct, while that cited in their Table III is in error by a factor of 10) and leads to the $\Delta G_f°$ values we have tabulated for the resulting aqueous species which may be represented by either $OsO_4(aq)$ or $H_2OsO_5(aq)$. The free energy leads to

$$Os(c) + 4H_2O(liq) = OsO_4(aq) + 8H^+(aq) + 8e^- \qquad E° = -0.84 \text{ v}$$

Sauerbrunn and Sandell (162) have investigated the ionization of aqueous solutions of OsO_4 (often called perosmic acid solutions). Their results, which shed no light on the extent of hydration of aqueous OsO_4, are conveniently represented as

$$H_2OsO_5(aq) = H^+(aq) + HOsO_5^-(aq) \qquad Q_{1.0} = 1 \times 10^{-12}$$

$$HOsO_5^-(aq) = H^+(aq) + OsO_5^{-2}(aq) \qquad Q_{1.0} \cong 3 \times 10^{-15}$$

Free energies of $HOsO_5^-(aq)$ and OsO_5^{-2} (aq) are calculated from these values and the tabulated $\Delta G_f°$ for $H_2OsO_5(aq)$. The principal Os(VIII) species in 1 *M* OH^- solution is the singly charged anion, and we calculate the following potential for Os|Os(VIII) in such solutions.

$$Os(c) + 9OH^-(aq) = HOsO_5^-(aq) + 4H_2O(liq) + 8e^- \qquad E° = 0.0 \text{ v}$$

The potential measurements of Cartledge (37) led to

$$OsO_2 \cdot 2H_2O(c) = OsO_4(aq) + 4H^+(aq) + 4e^- \quad E° = -0.96 \text{ v}$$

Similar measurements with OsO_2 led (37) to a slightly less negative potential (−0.95 v) for the $OsO_2|OsO_4$ couple and thence to the free energy for the less stable anhydrous dioxide. Free energies lead to the following potentials.

$$Os(c) + 4OH^-(aq) = OsO_2 \cdot 2H_2O(ppt) + 4e^- \qquad E° = 0.12 \text{ v}$$

$$Os(c) + 4H_2O(liq) = OsO_2 \cdot 2H_2O(ppt) + 4H^+(aq) + 4e^- \qquad E° = -0.72 \text{ v}$$

$$OsO_2 \cdot 2H_2O(ppt) + 5OH^-(aq) = HOsO_5^-(aq) + 4H_2O(liq) + 4e^- \qquad E° = -0.10 \text{ v}$$

High-temperature equilibrium measurements on the disproportionation of $OsO_2(c)$ to Os(c) and $OsO_4(g)$ have led to a reported (136) $\Delta H_f° = -64$ kcal mole^{-1} for $OsO_2(c)$. Combination of this $\Delta H_f°$ with $\Delta G_f° = -46$ kcal mole^{-1} leads to a negative $S_{298}°$ for $OsO_2(c)$. It may be that there are large errors in the $\Delta H_f°$ or $\Delta G_f°$ or in both, but we choose to omit the $\Delta H_f°$ from Table III.

TABLE III

THERMODYNAMIC DATA FOR OSMIUM AT 298°K[a]

Substance	$\Delta H_f°$, kcal mole^{-1}	$\Delta G_f°$, kcal mole^{-1}	$S°$, cal deg^{-1} mole^{-1}
Os(c)	0	0	7.8^{112}
Os(g)	$188^{36,145}$	177	46.0^{112}
$OsO_2(c)$		-46^{37}	
$OsO_2 \cdot 2H_2O(ppt)$		-161^{37}	
OsO_4(c, yellow)	-94^{195}	-73	35^{110}
OsO_4(c, white)	-92^{110}	-73^{142}	39^{110}
$OsO_4(g)$	-81^{110}	-70^{110}	70.3^{167}
$OsO_4(aq)$		-72^{2}	
$H_2OsO_5(aq)$		-129^{2}	
$HOsO_5^-(aq)$		-113^{162}	
$OsO_5^{-2}(aq)$		-93^{162}	
$OsS_2(c)$	$-35^{108,205}$	$-32^{108,205}$	$13^{108,205}$
$OsF_6(g)$			85.6^{202}
$OsF_6(c)$			$61^{34,202}$
$OsCl_4(c)$	-61^{114}	-38^{114}	37^{114}
$OsCl_3(c)$	-46^{115}	-29^{115}	31^{115}
$K_2OsCl_6(c)$	$\sim -284^{153}$		
$Na_2OsCl_6(c)$	$\sim -265^{153}$		
$BaOsCl_6(c)$	$\sim -266^{153}$		

[a] Superscript numbers are references.

On the basis of new calculations (205) with high-temperature decomposition pressure data (108), we adopt the values cited in Table III for $OsS_2(c)$.

High-temperature equilibrium data (153) lead to the approximate heats of formation tabulated for $K_2OsCl_6(c)$, $Na_2OsCl_6(c)$, and $BaOsCl_6(c)$.

For $OsF_6(g)$ we have $S°_{298} = 85.6$ cal deg^{-1} mole^{-1} from molecular constants (202). Vapor pressure data (34) permit calculation of $\Delta S°$ of sublimation of the solid and thence calculation of $S°_{298} = 61$ cal deg^{-1} mole^{-1} for $OsF_6(c)$. Vapor pressure data (35) are also available for OsF_5, but we know of no other thermodyamic data for this or any other fluoride of osmium.

High-temperature equilibrium data (114, 115) lead to the tabulated values for $OsCl_3(c)$ and $OsCl_4(c)$.

Latimer (118) has estimated $E° = (-0.85 \text{ v})$ for the $OsCl_6^{-3}|OsCl_6^{-2}$ couple. Mertes, Crowell, and Brinton (127) have made cell measurements with fairly concentrated HBr solutions (2–4 *M*) and report the following.

$$OsBr_6^{-3}(aq) = OsBr_6^{-2}(aq) + e^- \quad E(2.1\ M\ \text{HBr}) = -0.349\ \text{v}$$

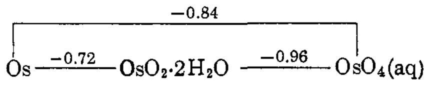
The potential is less negative at higher concentrations of HBr. Others (61, 62) have reported $E° = -0.45$ v for both the $OsCl_6^{-3}|OsCl_6^{-2}$ and $OsBr_6^{-3}|OsBr_6^{-2}$ couples. It is probable that the various osmium halide species are hydrolyzed in their dilute solutions so that these latter potentials should apply to such species as $OsO^+(aq)$ and $OsO^{+2}(aq)$.

Buckingham, Dwyer, and Sargeson (30) have reported potentials for 31 couples involving organic complexes of Os(II) and Os(III). Again, we are unable to calculate free energies.

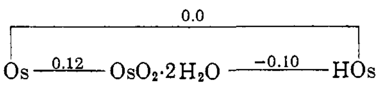
Potential diagrams for osmium are given in Scheme II.

SCHEME II

ACIDIC SOLUTION



BASIC SOLUTION



IV. RHODIUM

A. DESCRIPTIVE CHEMISTRY

The chemistry of rhodium involves a variety of species that contain rhodium in oxidation states ranging from −1 to +6, with the +1 and +3 states being the most common.

Finely divided rhodium can be dissolved in aqua regia or hot concentrated sulfuric acid. The oxide Rh_2O_3 is formed when the metal is heated with oxygen above 600°. Reactions of rhodium with chlorine (~400°) and with fluorine (~550°) yield $RhCl_3$ and RhF_3. Reaction of the metal with a melt of KOH and KNO_3 is believed to yield $RhO_2(c)$, while reaction with a melt of $KHSO_4$ yields $Rh_2(SO_4)_3$.

Our discussion begins with Rh(VI) and Rh(V) and proceeds toward lower oxidation states. A yellow hexafluoride and a red pentafluoride have been reported. Both Rh(V) and Rh(VI) have been reported to exist in solutions of Rh(III) that have been oxidized by hypobromite, but these high-oxidation-state species are poorly characterized.

In addition to the already mentioned $RhO_2(c)$, hydrous RhO_2 is believed to form when Rh(III) is treated with strong oxidizing agents in basic solution. The hydrous oxide represented by $RhO_2(hyd)$ decomposes to Rh_2O_3 when heated. Compounds of the type $M_2{}^I[RhX_6]$ (X = F, Cl) have been prepared. Treating $RhCl_3$ with liquid BrF_3 and then heating the resulting $RhF_4 \cdot 2BrF_3$ yields RhF_4.

The hydrate $Rh_2O_3 \cdot 5H_2O$ is precipitated when base is added to aqueous Rh(III). It dissolves in acid to yield $Rh(H_2O)_6{}^{+3}(aq)$. Solid RhF_3, $RhCl_3$, and RhI_3 are known. The hydrated salt $RhCl_3 \cdot 4H_2O$ is often the starting compound in the synthetic chemistry of rhodium. It can be prepared by evaporating a solution made by dissolving hydrous Rh_2O_3 in hydrochloric acid. Although $RhCl_3 \cdot 4H_2O$ is very soluble in water, it does not yield a precipitate immediately on addition of silver ion. When $Rh(H_2O)_6{}^{+3}(aq)$ is heated with hydrochloric acid, ions ranging from $RhCl(H_2O)_5{}^{+2}$ to $RhCl_6{}^{-3}$ are formed, depending on the chloride concentration. The complex ions $RhF_6{}^{-3}(aq)$ and $Rh(NH_3)_6{}^{+3}(aq)$ are also known, as are mixed complexes involving amine type ligands. Rhodium(III) sulfates are known to exist as several definite hydrates.

Rhodium(II) occurs infrequently, but compounds of the type $[Rh(py)_6]X_2$ (X = halide) have been established. The oxide RhO has been reported to exist at high temperatures.

A number of organic complexes of Rh(I) have been prepared (48). The oxide Rh_2O is believed to exist at high temperatures. Carbonyl compounds of Rh(I) are $[Rh(CO)_2Cl]_2$ and $\pi\text{-}C_5H_5Rh(CO)_2$.

Compounds of Rh(0) all involve carbonyls: $[Rh(CO)_4]_2$ and $Rh_6(CO)_{16}$. Rhodium in the −1 oxidation state also involves a carbonyl, $Rh(CO)_4{}^-$.

For a more extensive discussion of descriptive chemistry of rhodium, see the review by Shukla (186).

B. THERMOCHEMISTRY

We now consider thermodynamic data relevant to rhodium and its compounds. We adopt the entropies of Rh(c) and Rh(g) tabulated by Kelley and King (112). Four investigations (8, 58, 96, 144) of the heat of sublimation of rhodium are in good agreement with $\Delta H°_{298} = 133$ kcal mole^{-1}. Combination of this value with the entropies leads to $\Delta G_f°$ for Rh(g).

Two older studies (207, 208) on the oxides of rhodium involved vapor pressure measurements and measurements of the heats of reduction by hydrogen. However, the various phases do not appear to have been properly identified. The values we cite in Table IV for $Rh_2O_3(c)$ are based (with an estimated $\Delta C_p°$) on the recent vapor pressure study of Schmahl and Minzl (168).

Hoare (100) has made electrochemical measurements on rhodium electrodes with films of adsorbed oxygen. Interpretation of his results in terms of surface films of RhO and Rh_2O_3 on Rh leads to the following potentials.

TABLE IV

THERMODYNAMIC DATA FOR RHODIUM AT 298°K[a]

Substance	ΔH_f°, kcal mole^{-1}	ΔG_f°, kcal mole^{-1}	S°, cal deg^{-1} mole^{-1}
Rh(c)	0	0	7.53[112]
Rh(g)	133[8,58,96,144]	122	44.39[112]
Rh^{+3}(aq)		(46)[69,148]	
RhO(surf.)		−19[100]	
Rh_2O_3(c)	∼−83[168]	∼−65[168]	∼27[168]
Rh_2O_3(surf.)		−48[100]	
$Rh(OH)_3$(c)		(−112)	
$RhOH^{+2}$(aq)		(−6)[69,148]	
RhO^{+2}(aq)		(22)[64,95]	
RhO_4^{-2}(aq)		(−78)[93,95]	
RhF_6(g)			∼82.0[182]
$RhCl_6^{-3}$(aq)	−204[73]	(−154)[50]	∼46
$RhCl_6^{-2}$(aq)		(−126)	
$RhCl_3$(c)	72[21]	54[21]	27[21]
Na_3RhCl_6(c)	−368[73]		
$Na_3RhCl_6 \cdot 12H_2O$(c)	−1216[73]		
K_3RhCl_6(c)	∼−369[153]		
$Ba_3(RhCl_6)_2$(c)	∼−716[74]		

[a] Superscript numbers are references.

$$\mathrm{Rh(c) + H_2O(liq) = RhO(surf.) + 2H^+(aq) + 2e^-} \qquad E^\circ = -0.81 \text{ v}$$

$$\mathrm{2Rh(c) + 3H_2O(liq) = Rh_2O_3(surf.) + 6H^+(aq) + 6e^-} \qquad E^\circ = -0.88 \text{ v}$$

The first potential leads to $\Delta G_f^\circ = -19$ kcal mole^{-1} for RhO(surf.), while the second potential leads to $\Delta G_f^\circ = -48$ kcal mole^{-1} for Rh_2O_3(surf.), which is considerably less negative than the value cited in Table IV for Rh_2O_3(c). It may be that the surface species of Rh(III) is less stable than Rh_2O_3(c), or it may be that one or both of the calculated free energies is in error.

Investigations of the solubility (69) of $Rh(OH)_3$ and the hydrolysis (69, 148) of Rh^{+3} lead to the following.

$$\mathrm{Rh^{+3}(aq) + H_2O(liq) = RhOH^{+2}(aq) + H^+(aq)} \qquad K = 5 \times 10^{-4}$$

$$\mathrm{Rh(OH)_3(c) = RhOH^{+2}(aq) + 2OH^-(aq)} \qquad K = 5 \times 10^{-23}$$

$$\mathrm{Rh(OH)_3(c) = Rh^{+3}(aq) + 3OH^-(aq)} \qquad K_{sp} = 1 \times 10^{-33}$$

By comparison with data for other $M_2O_3|M(OH)_3$ pairs, we estimate $\Delta G^\circ \cong (10)$ kcal for hydration of Rh_2O_3 and calculate $\Delta G_f^\circ \cong (-112)$ kcal mole^{-1} for $Rh(OH)_3$(c), which leads to

$$\mathrm{Rh(c) + 3OH^-(aq) = Rh(OH)_3(c) + 3e^-} \qquad E^\circ = (0.0) \text{ v}$$

Combination of the ΔG_f° of $Rh(OH)_3$(c) with the ΔG° calculated from the solubility product above leads to $\Delta G_f^\circ \cong (46)$ kcal mole^{-1} for Rh^{+3}(aq) and thence to

$$\mathrm{Rh(c) = Rh^{+3}(aq) + 3e^-} \qquad E^\circ = (-0.7) \text{ v}$$

With the stability constant (50) for $RhCl_6^{-3}$(aq), we calculate its $\Delta G_f^\circ \cong (-154)$ kcal mole^{-1} and thence

$$\mathrm{Rh(c) + 6Cl^-(aq) = RhCl_6^{-3}(aq) + 3e^-} \qquad E^\circ = (-0.5) \text{ v}$$

Gire (73) has measured the heat of reduction of $RhCl_6^{-3}$(aq) to Rh(c) by means of Co(c). Using his results, we calculate $\Delta H_f^\circ = -204$ kcal mole^{-1} for $RhCl_6^{-3}$(aq). Combination of this heat with the free energy of formation leads to $\bar{S}_2^\circ \cong 46$ cal deg^{-1} mole^{-1} for $RhCl_6^{-3}$(aq), a value which appears to be reasonable. The heats of solution (73) of Na_3RhCl_6(c) and $Na_3RhCl_6 \cdot 12H_2O$(c) permit us to calculate their heats of formation.

Dwyer and Schafer (64) have reported potentials for the Rh(III)|Rh(IV) couple in sulfuric acid solutions. Their potentials are in good agreement with the results of Grube and Gu (95) for the Rh(III)|Rh(IV) couple in nitric acid. Grube and Gu (95) have also investigated the Rh(IV)|Rh(VI) couple, while Grube and Autenrieth (93) have investigated the Rh(III)|Rh(VI) couple. Although the species characteristic of these higher oxidation states have not been well established, we follow Latimer (118) and others in describing them as RhO^{+2} and RhO_4^{-2}. On this basis, we write the couples mentioned above as follows, with our standard potentials estimated from the reported potentials.

$$\mathrm{Rh^{+3}(aq) + H_2O(liq) = RhO^{+2}(aq) + 2H^+(aq) + e^-} \qquad E^\circ \cong -1.4 \text{ v}$$

$$\mathrm{Rh^{+3}(aq) + 4H_2O(liq) = RhO_4^{-2}(aq) + 8H^+(aq) + 3e^-} \qquad E^\circ \cong -1.5 \text{ v}$$

$$\mathrm{RhO^{+2}(aq) + 3H_2O(liq) = RhO_4^{-2}(aq) + 6H^+(aq) + 2e^-} \qquad E^\circ \cong -1.5 \text{ v}$$

The only path presently available for evaluation of the free energies of RhO^{+2} and RhO_4^{-2} involves combination of the potentials above with the $\Delta G_f^\circ = (46)$ kcal mole^{-1} already cited for Rh^{+3}(aq).

Other approximate potentials we are able to calculate with the above information are the following.

$$\mathrm{Rh(c) + 8OH^-(aq) = RhO_4^{-2}(aq) + 4H_2O(liq) + 6e^-} \qquad E^\circ = (0.0) \text{ v}$$

$$\mathrm{Rh(OH)_3(c) + 5OH^-(aq) = RhO_4^{-2}(aq) + 4H_2O(liq) + 3e^-} \qquad E^\circ = (0.1) \text{ v}$$

$$\mathrm{Rh(c) + 4H_2O(liq) = RhO_4^{-2}(aq) + 8H^+(aq) + 6e^-} \qquad E^\circ = (-1.1) \text{ v}$$

Willis (206) has estimated a potential for cyanide complexes from his polarographic data.

$$\mathrm{Rh(CN)_6^{-4}(aq) = Rh(CN)_6^{-3}(aq) + e^-} \qquad E^\circ = (0.9) \text{ v}$$

We also have the estimated potential from Latimer (118) for the chloride complexes.

$$\mathrm{RhCl_6^{-3}(aq) = RhCl_6^{-2}(aq) + e^-} \qquad E^\circ = (-1.2) \text{ v}$$

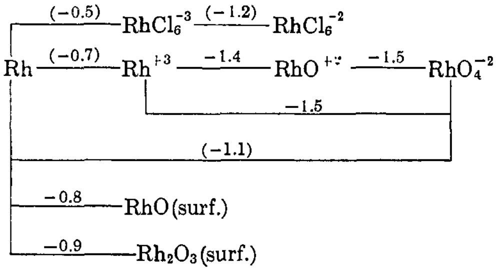
We have few thermodynamic data available for solid halides of rhodium. Of these, the most reliable appear to be the high-temperature equilibrium results of Bell, Tagmi, and Merten (21) for decomposition of $RhCl_3$. Their results lead to the values we tabulate for $RhCl_3$(c). Although earlier workers (153, 208) have reported data supposedly applicable to lower oxidation state chlorides, the work of Bell, Tagami, and Merten (21) indicates that RhCl and $RhCl_2$ do not exist as solids. Puche (153) has studied the thermal decomposition of K_3RhCl_6(c), from which data we obtain its $\Delta H_f°$. From a similar study (74) we also obtain $\Delta H_f°$ for $Ba_3(RhCl_6)_2$(c).

Murmann and Sullivan (129) reported an equilibrium quotient for formation of a [Np(V)–Rh(III)] complex as well as an approximate ΔH value.

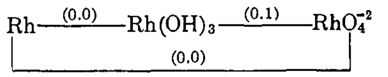
Much of the information give in this section is summarized by the potential diagrams in Scheme III.

SCHEME III

ACIDIC SOLUTION



BASIC SOLUTION



V. IRIDIUM

A. DESCRIPTIVE CHEMISTRY

The chemistry of iridium involves a variety of species that contain iridium in oxidation states ranging from 0 to +6.

Metallic iridium reacts with oxygen, fluorine, and chlorine to yield IrO_2 (~1050°), IrF_6 (~200°), and $IrCl_3$ (~600°). The sulfide IrS can be prepared by direct combination of the elements. A melt of KNO_3 and KOH reacts with the metal to give the sesquioxide, Ir_2O_3, while $Ir_2(SO_4)_3$ can be prepared with molten $KHSO_4$. The hexachloroiridate(IV), $M_2^{I}[IrCl_6]$, is formed when an alkali metal chloride is heated with Cl_2 and powdered iridium.

We begin our further discussion with the higher oxidation states. The only compounds of Ir(VI) appear to be IrF_6 and IrO_3(g), which is known at high temperatures. The hexafluoride reacts with water to yield IrO_2(hyd) and oxygen. The "pentafluoride" $(IrF_5)_4$ was formerly thought to be IrF_4. The compounds $M^{II}[IrF_6]_2$ react with water to yield IrF_6^{-2}(aq) and O_2.

As mentioned above, both IrO_2 and IrO_2(hyd) are known. The hydrate is soluble in acid but insoluble in base. When anhydrous IrO_2 is dissolved in excess hydrochloric acid, H_2IrCl_6 is formed. Hydrated $IrCl_4$ can be prepared by treating $(NH_4)_2IrCl_6$ with aqua regia. Compounds of the type $M_2^{I}IrX_6$ (X = F, Cl, Br) are soluble in water. The ions $[IrCl_3(H_2O)_3]^+$ and $[IrCl_4(H_2O)_2]$ have been identified in aqueous solution. A sulfide IrS_2 is also known.

Iridium is most commonly found in the +3 oxidation state. The oxide Ir_2O_3 also exists as a hydrate, which may be partially air oxidized to IrO_2(hyd). A sulfide Ir_2S_3 is known. The trifluoride IrF_3 is obtained by reduction of IrF_6. The trichloride exists in a brown form and a red form, neither of which dissolves in water. Several hydrates of $IrCl_3$ are known, all of which dissolve in water to give acidic solutions containing anionic complexes. Other halide hydrates such as $IrBr_3 \cdot 4H_2O$ and $IrI_3 \cdot 3H_2O$ are prepared from Ir_2O_3(hyd) with the appropriate hydrohalic acid. Compounds of types $M_3^{I}IrX_6$ and $M_2^{I}[IrX_5(H_2O)]$ are obtained by reduction of the corresponding haloiridate(IV).

The dihalides $IrCl_2$, $IrBr_2$, and IrI_2 are products of the thermal decomposition of the corresponding trihalide. As already mentioned, IrS results from the direct combination of the elements. Iridium(II) is also known in compounds such as $K_4[Ir(CN)_6]$ and $K_6[Ir(SO_3)_4] \cdot 10H_2O$.

Like the dihalides, IrCl, IrBr, and IrI can be obtained by thermal decomposition of the appropriate trihalide. All three monohalides are insoluble in acid and alkali. Other Ir(I) compounds are $IrClCO(PPh_3)_2$ and $IrClCO(PEt_3)_2$.

Known carbonyls are $[Ir(CO)_4]_2$ and $[Ir(CO)_3]_x$. The compound $Ir(NH_3)_5$, which is stable at room temperature, is prepared by treating $[Ir(NH_3)_5Br]Br_2$ with potassium in liquid ammonia.

B. THERMOCHEMISTRY

We now consider thermodynamic data for iridium and its compounds. We adopt the entropies of Ir(c) and Ir(g) tabulated by Kelley and King (112). Three determinations (96, 144, 146) of the heat of sublimation of Ir(c) are in good agreement with $\Delta H°_{298}$ = 160 kcal $mole^{-1}$. Combination of the entropies with the heat of sublimation leads to $\Delta G_f°$ for Ir(g).

The results of several investigators are not in good agreement concerning IrO_2(c). Tabulations by Brewer (27) and NBS Circular 500 (160) are based on data from the old German literature, and the values they adopted are $\Delta H_f°$ = −44 and −40 kcal $mole^{-1}$, respectively, for IrO_2(c). The more recent results of Cordfunke and Meyer (47) lead to $\Delta H_f° = -65.5 \pm 1.5$ kcal $mole^{-1}$ for IrO_2(c). These workers claim that a nonstoichiometric oxide becomes important at high temperatures, but Bell, Tagami, and Inyard (20) have contradicted this claim. The results of Bell, Tagami, and Inyard (20) and Schäfer and Heitland (164) appear to be the most reliable and are in reasonable agreement. The values we list in Table V are averages of the results obtained by these latter workers (20, 164).

TABLE V

THERMODYNAMIC DATA FOR IRIDIUM AT 298°K[a]

Substance	$\Delta H_f°$, kcal mole^{-1}	$\Delta G_f°$. kcal mole^{-1}	$S°$, cal deg^{-1} mole^{-1}
Ir(c)	0	0	8.48[112]
Ir(g)	160[96.144.146]	149	46.24[112]
IrO(surf.)		−17[101]	
IrO_2(c)	−55[20.164]	−42[20.164]	15[20.164]
IrO_2(surf.)		−27[101]	
IrO_3(g)	3[18]	7[18]	69[18]
Ir_2S_3(c)	∼−58[24.205]	∼−53[24.205]	∼23[24,205]
IrS_2(c)	∼−34[24.205]	∼−32[24,205]	∼15[24,205]
IrF_6(c)			60[34]
IrF_6(g)			84[112,190]
$IrCl_3$(c)	−61[19]	−43[19]	27[19]
$IrCl_3$(g)	25[18]	24[18]	90[18]
$IrCl_6^{-3}$(aq)	∼−148[78]	∼−129	(50)
$IrCl_6^{-2}$(aq)	∼−179[70]	∼−109	∼(70)[70]
K_3IrCl_6(c)	∼−367[78]		
K_2IrCl_6(c)	∼−281[72]		

[a] Superscript numbers are references.

Potential measurements by Hoare (101) lead to the following.

$$Ir(c) + H_2O(liq) = IrO(surf.) + 2H^+(aq) + 2e^- \qquad E° = -0.87 \text{ v}$$

$$Ir(c) + 2H_2O(liq) = IrO_2(surf.) + 4H^+(aq) + 4e^- \qquad E° = -0.94 \text{ v}$$

These potentials lead to the $\Delta G_f°$ values listed in Table V for IrO(surf.) and IrO_2(surf.).

For IrO_3(g) we adopt the results of Bell and Tagami (18), who have also summarized the results of previous workers. They (18, 19) have also determined the values we tabulate for $IrCl_3$(c) and $IrCl_3$(g). Bell and Tagami (19) have criticized the work of Wöhler and Streicher (209), who presented values for the heat of formation of IrCl(c), $IrCl_2$(c), and $IrCl_3$(c).

Heat capacities and vapor pressures have been used in calculating (205) the values cited in Table V for Ir_2S_3(c) and IrS_2(c).

On the basis of two statistical calculations (112, 190), we adopt $S°_{298}$ = 84 cal deg^{-1} mole^{-1} for IrF_6(g). Combination of this entropy with vapor pressure data (34) leads to $S°_{298}$ = 60 cal deg^{-1} mole^{-1} for IrF_6(c).

The work of George, Hanania, and Irvine (70) appears to be the most reliable for the following.

$$IrCl_6^{-3}(aq) = IrCl_6^{-2}(aq) + e^- \qquad E° = -0.867 \text{ v}$$

Potentials at other temperatures (70) also lead to a $\Delta H°$ value and to $\bar{S}_2°(IrCl_6^{-3}) - \bar{S}_2°(IrCl_6^{-1}) = -19.6$ cal deg^{-1} mole^{1}. More negative potentials (91, 116, 152) for the above couple are probably due to higher ionic strengths of the solutions.

We obtain $\Delta H_f° \cong -281$ kcal mole^{-1} for K_2IrCl_6(c) from high-temperature equilibrium data (72). The heat of solution (73) of K_2IrCl_6(c) then leads to $\Delta H_f° \cong -148$ kcal mole^{-1} for $IrCl_6^{-2}$(aq). Next, the $\Delta H°$ associated with the $IrCl_6^{-3}|IrCl_6^{-2}$ couple (70) permits calculation of $\Delta H_f° = -179$ kcal mole^{-1} for $IrCl_6^{-3}$(aq). We estimate entropies of $IrCl_6^{-3}$(aq) and $IrCl_6^{-2}$(aq) that are consistent with the difference cited above and combine with the $\Delta H_f°$ values to find the free energies given in Table V. These free energies lead to the following potentials.

$$Ir(c) + 6Cl^-(aq) = IrCl_6^{-3}(aq) + 3e^- \qquad E° = -0.86 \text{ v}$$

$$Ir(c) + 6Cl^-(aq) = IrCl_6^{-2}(aq) + 4e^- \qquad E° = -0.86 \text{ v}$$

We calculate $\Delta H_f°$ for K_3IrCl_6(c) from its heat of solution (73) and $\Delta H_f°$ values for the ions.

Dwyer, McKenzie, and Nyholm (63) have reported the potential

$$IrBr_6^{-3}(aq) = IrBr_6^{-2}(aq) + e^- \qquad E° = -0.99 \text{ v}$$

This value is in good agreement with that reported by Ptitsyn (152), who has also reported the following.

$$IrI_6^{-3}(aq) = IrI_6^{-2}(aq) + e^- \qquad E(1\ M\ \text{KI}) = -0.49 \text{ v}$$

Chang and Garner (38) have found the following potentials.

$$IrCl_5^{-2}(aq) = IrCl_5^-(aq) + e^- \qquad E(0.2\ M\ \text{HNO}_3) \cong -1.0 \text{ v}$$

$$IrCl_4^-(aq) = IrCl_4(aq) + e^- \qquad E(0.4\ M\ \text{HNO}_3) \cong -1.2 \text{ v}$$

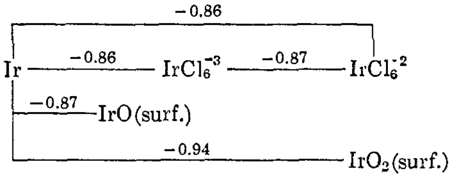
This latter potential is in agreement with the value reported by El-Awady, Bounsall, and Garner (65), who also report

$$IrCl_3(aq) = IrCl_3^+(aq) + e^- \qquad E(0.4\ M\ \text{HClO}_4) = -1.30 \text{ v}$$

Some potentials for iridium are summarized in Scheme IV.

SCHEME IV

ACIDIC SOLUTION



VI. PALLADIUM

A. DESCRIPTIVE CHEMISTRY

Unlike the elements previously discussed in this review, palladium is known to exist in only three oxidation states: 0, +2, and +4. We start with a summary of reactions of the element.

Elemental palladium reacts with oxygen and sulfur to yield PdO and PdS, respectively. The monoxide is also prepared by heating the metal with a melt of KOH and KNO_3, while $PdSO_4$ is obtained from a melt of $KHSO_4$. The element reacts with the halogens to form $Pd[PdF_6]$, $PdCl_2$, and (in presence of HNO_3) $PdBr_2$. Hot concentrated nitric acid reacts with the metal to give $Pd(NO_3)_2$, while $M_2[PdCl_6]$ compounds are obtained by treating the metal with hot aqua regia in the presence of excess MCl.

We begin our discussion of the positive oxidation states with Pd(IV). The tetrafluoride PdF_4 can be prepared by heating $Pd[PdF_6]$ with fluorine at high pressure. The fusion of PdS with sulfur yields PdS_2, while if sodium carbonate is present the thiopalladate Na_2PdS_3 is obtained. The diselenide and ditelluride are also known. In addition to the hexachloropalladates $M_2[PdCl_6]$ mentioned above, the corresponding fluoride, bromide, and iodide compounds are known. Hydrous dioxide PdO_2(hyd) is formed as a precipitate when solutions containing $PdCl_6^{-2}$ are treated with alkali metal hydroxide. The hydrous dioxide is soluble in both dilute acid and concentrated base. Some complexes of the type $[Pd(py)_2Cl_2]Cl_2$ have been reported.

The "trifluoride" $Pd[PdF_6]$ was long thought to be an example of palladium in the +3 oxidation state until Bartlett and Rao (11) showed that the compound contains palladium in the +2 and +4 oxidation states.

Many compounds of Pd(II) can be prepared by reactions involving the element. Hydrous monoxide is obtained when $Pd(NO_3)_2$ is hydrolyzed. The difluoride PdF_2 results when $Pd(NO_3)_2$ is treated with HF. Addition of iodide ion to a solution of $PdCl_2$ is reported to yield the diiodide as a precipitate. Many four-coordinate complexes of types PdX_4^{-2} (X = Cl, Br, I, CN, NO_2, SCN) and PdL_4^{+2} (L = various amines), as well as mixed complexes, are known to exist in aqueous media. The salt $[Pd(NH_3)_4][Pd(SCN)_4]$ is known.

Several compounds involving palladium in the zero oxidation state are known. Examples are $Pd(CNR)_2$ (R = phenyl, etc.), $Pd(diars)_2$, $Pd(PAr_3)_4$, and $Pd(PF_3)_4$.

B. THERMOCHEMISTRY

We now turn to detailed consideration of thermodynamic properties of palladium and its compounds. For Pd(c) and Pd(g) we adopt entropies tabulated by Kelley and King (112). Results of several workers (8, 57, 97, 138, 194, 212) for the heat of sublimation of Pd(c) are in good agreement with $\Delta H^\circ_{298} = 91$ kcal mole^{-1}. Combination of this value with the entropies leads to ΔG_f° for Pd(g).

Nace and Aston (130) have studied the thermodynamics of the palladium–hydrogen system and have summarized previous work. The values in Table VI for Pd_2H(c) are based on their work.

On the basis of their vapor pressure study, Bell, Inyard, and Tagami (15) report $\Delta H_f^\circ = -26.8 \pm 2.0$ kcal mole^{-1} and $S^\circ_{298} = 9.9 \pm 2.0$ cal deg^{-1} mole^{-1} for PdO(c). They have also summarized data from the older literature and cite values ranging from −20 to −26 kcal mole^{-1} for ΔH_f° of PdO(c). Warner (199), from results of similar high-temperature experiments, reports $\Delta H_f^\circ = -28.35 \pm 0.4$ kcal mole^{-1} and $S^\circ_{298} = 8.60 \pm 0.3$ cal deg^{-1} mole^{-1} for PdO(c). Schmahl and Minzl (169) also report decomposition vapor pressures for PdO(c). We have used their data with heat capacity equations tabulated by Kelley (111) to calculate $\Delta H_f^\circ = -27.5$ kcal mole^{-1} and $S^\circ_{298} = 9.3$ cal deg^{-1} mole^{-1} for PdO(c). In Table VI we list averages from these three investigations. No third-law entropy for PdO(c) is available.

We have used high-temperature equilibrium data from Niwa, Yokokawa, and Isoya (137) and from Biltz and Laar (23) in calculating ΔH_f° values for Pd_4S, PdS, and PdS_2.

Third-law entropies (92, 205) for tellurides of palladium and high-temperature equilibrium data (189) for decomposition of $PdTe_2$ to PdTe have been reported.

Decomposition pressures (16, 141, 153) of Cl_2(g) over $PdCl_2$(c) at high temperatures lead, with ΔC_p° estimated from the analogous reaction for $NiCl_2$(c), to the values of the thermodynamic properties we tabulate for $PdCl_2$(c). Bell, Merten, and Tagami (16) and Oranskaya and Mikhailova (141) have also determined values for the heat and entropy of formation of $PdCl_2$(g) at high temperatures, but their agreement is poor and we choose not to tabulate any values.

On the basis of their potential measurements, Izatt, Eatough, and Christensen (104) report $E^\circ = -0.915 \pm 0.005$ v for the $Pd|Pd^{+2}$ couple. They (104) have also adjusted the value reported by Templeton, Watt, and Garner (191) to zero ionic strength to obtain $E^\circ = -0.945$ v for the $Pd|Pd^{+2}$ couple. We write

$$Pd(c) = Pd^{+2}(aq) + 2e^- \qquad E^\circ = -0.92 \text{ v}$$

and calculate $\Delta G_f^\circ = 42.4$ kcal mole^{-1} for Pd^{+2}(aq).

Templeton, Watt, and Garner (191) and Fasman, Kutyukov, and Sokol'skii (68) have reported E(1 M HCl) = −0.62 and −0.59 v and E(1 M KCl) = −0.60 v for the $Pd|PdCl_4^{-2}$ couple. More recently, Kravtsov and Zelenskii (117) have also reported E(1 M HCl) = −0.59 v for this couple. Stepwise formation constants for the ions $PdCl_n^{2-n}$(aq) [n = 1–4] have been determined many times (25, 32, 33, 59, 84, 174, 183) with the investigations that appear to be most reliable centering on $\log \beta_4 = 11$. Combination of this value with the above $Pd|Pd^{+2}$ potential leads to

$$Pd(c) + 4Cl^-(aq) = PdCl_4^{-2}(aq) + 2e^- \qquad E^\circ = -0.59 \text{ v}$$

The corresponding $\Delta G_f^\circ = -98$ kcal mole^{-1} for $PdCl_4^{-2}$(aq) is listed in Table VI. The chemical equilibrium and potential data for $PdCl_4^{-2}$(aq) and Pd^{+2}(aq) are in satisfactory agreement.

Calorimetric data from Thomsen (193) allow us to calculate $\Delta H_f^\circ = -127$ and −131 kcal mole^{-1} for $PdCl_4^{-2}$(aq). Later discussions of these results from Thomsen (193) will be in terms of an average $\Delta H_f^\circ = -129$ kcal mole^{-1}. More recently, Templeton, Watt, and Garner (191) have measured $Pd|PdCl_4^{-2}$ potentials at several temperatures. Their data lead to $\Delta H_f^\circ =$

TABLE VI

THERMODYNAMIC DATA FOR PALLADIUM AT 298°K[a]

Substance	$\Delta H_f°$, kcal mole^{-1}	$\Delta G_f°$. kcal mole^{-1}	$S°$, cal deg^{-1} mole^{-1}
$Pd(c)$	0	0	9.06[112]
$Pd(g)$	91[8,57,97,138,194,212]	82	39.90[112]
$Pd^{+2}(aq)$	~42[105,106,191]	42.4[104,191]	~−25
$Pd_2H(c)$	−4.7[130]	−1.2[130]	21.9[130]
$PdO(c)$	−27.6[15,111,169,199]	−20.3[15,111,169,199]	9.3[15,111,169,199]
$PdO(g)$	83[138]	78[138]	52[138]
$Pd(OH)_2(c)$	−88[106,193]	−72[104]	~36 (?)
$Pd(OH)_2$(surf.)		−65[163]	
$Pd(OH)_2(aq)$		−68[104]	
$Pd(OH)^+(aq)$		−13[104]	
$Pd(OH)_4(c)$	−155[193]	−115	(35)
$Pd_4S(c)$	~−16[137]		
$PdS(c)$	~−18[137]		
$PdS_2(c)$	~−19[23]		
$PdTe(c)$			21.4[92]
$PdTe_2(c)$			30.3[205]
$PdCl_2(c)$	~−39[16,141,153]	~−28[16,141,153]	~26[16,141,153]
$PdCl_4^{-2}(aq)$	−125[191]	−98	~56
$PdCl_6^{-2}(aq)$		−103[91,204]	
$K_2PdCl_4(c)$	−259[193]		
$K_2PdCl_6(c)$	~−277[153]	−246[170]	~95
$Pd(NH_3)_2Cl_2(c)$	~−101[103]		
$Pd(NH_3)_4Cl_2(c)$	~−154[103]		
$Pd(N_3)_2Cl_2^{-2}(aq)$		144[184]	
$PdBr_2(c)$	~−25[106]		
$PdBr_4^{-2}(aq)$	−86[106]	−77[68,84,150,170,175]	~83
$PdBr_6^{-2}(aq)$		−81[91]	
$PdI_2(c)$	−14[106,179,193]	−14[179]	38[179]
$PdI_4^{-2}(aq)$		−41[68,84]	
$PdI_6^{-2}(aq)$		−44[91]	
$Pd(NH_3)_2I_2(c)$	~−70[103]		
$Pd(NH_3)_4I_2(c)$	~−118[103]		
$Pd(NH_3)_4^{+2}(aq)$		−25[85]	
$Pd(CN)_2(c)$	~−55[106]		
$Pd(SCN)_4^{-2}(aq)$		95[68,84]	
$Pd(NO_2)_4^{-2}(aq)$		−20[68]	

[a] Superscript numbers are references.

−125 kcal mole^{-1} for $PdCl_4^{-2}(aq)$. Still more recent calorimetric measurements by Izatt, Watt, Eatough, and Christensen (105) have led to reported $\Delta H°$ values for reduction of $Pd^{+2}(aq)$ to $Pd(c)$ by $I^-(aq)$ and for formation of $PdCl_4^{-2}(aq)$ from the ions. These results lead to $\Delta H_f° = -113$ kcal mole^{-1} for $PdCl_4^{-2}(aq)$.

For subsequent calculations we adopt $\Delta H_f° = -125$ kcal mole^{-1} for $PdCl_4^{-2}(aq)$ from the work of Templeton, Watt, and Garner (191). There are several reasons for this partly arbitrary choice. First, the adopted $\Delta H_f°$ will later lead to entropies for $Pd^{+2}(aq)$ and $Pd(OH)_2(c)$ that appear to be more reasonable than entropies derived from the rejected $\Delta H_f°$ values. Second, the adopted $\Delta H_f°$ leads to more consistent $\Delta H_f°$ values for several other compounds and ions. Third, the stoichiometry of the Pd^{+2}–I^- reaction (105) appears to us to be uncertain.

Combination of the adopted $\Delta H_f°$ with $\Delta G_f°$ leads to $\bar{S}_2° \cong 56$ cal deg^{-1} mole^{-1} for $PdCl_4^{-2}(aq)$.

Thomsen's (193) heat of solution of $K_2PdCl_4(c)$ permits us to calculate $\Delta H_f° \cong -259$ kcal mole^{-1} for $K_2PdCl_4(c)$.

Izatt, Watt, Eatough, and Christensen (105) have reported $\Delta H° = -5.5$ kcal for

$$Pd^{+2}(aq) + 4Cl^-(aq) = PdCl_4^{-2}(aq)$$

We use this $\Delta H°$ with our adopted $\Delta H_f°$ for $PdCl_4^{-2}(aq)$ in calculating $\Delta H_f° = 40$ kcal mole^{-1} for $Pd^{+2}(aq)$. Combination of this $\Delta H_f°$ with the $\Delta G_f°$ leads to $\bar{S}_2° = -30$ cal deg^{-1} mole^{-1} for $Pd^{+2}(aq)$. The rejected $\Delta H_f°$ values for $PdCl_4^{-2}(aq)$ lead to values of +10 and −44 cal deg^{-1} mole^{-1} for this entropy. Another path to this entropy involves combination of $\Delta H_f° = -86$ kcal mole^{-1} for $PdBr_4^{-2}(aq)$ from old calorimetric results of Joannis (106) with the recent (105) $\Delta H° = -13.1$ kcal for

$$Pd^{+2}(aq) + 4Br^-(aq) = PdBr_4^{-2}(aq)$$

These data lead to $\Delta H_f° = 43$ kcal mole^{-1} and thence to $\bar{S}_2° = -20$ cal deg^{-1} mole^{-1} for $Pd^{+2}(aq)$. We adopt average values of $\Delta H_f° = 42$ kcal mole^{-1} and $\bar{S}_2° \cong$

-25 cal deg^{-1} mole^{-1} for $Pd^{+2}(aq)$. This entropy for $Pd^{+2}(aq)$ *appears* to be more reasonable than those derived from the data we have rejected.

Potential data (68) lead to $\Delta G_f° = -75$ kcal mole^{-1} for $PdBr_4^{-2}(aq)$, while stability constants (84, 150, 170, 175) lead to $\Delta G_f°$ values ranging from -75 to -79 kcal mole^{-1}. We adopt $\Delta G_f° \cong -77$ kcal mole^{-1} for $PdBr_4^{-2}(aq)$ and calculate the following.

$$Pd(c) + 4Br^-(aq) = PdBr_4^{-2}(aq) + 2e^- \qquad E° \cong -0.49 \text{ v}$$

$$Pd^{+2}(aq) + 4Br^-(aq) = PdBr_4^{-2}(aq) \qquad \log \beta_4 = 15$$

Combination of data cited above leads to $\bar{S}_2° \cong 83$ cal deg^{-1} mole^{-1} for $PdBr_4^{-2}(aq)$.

From the work of Grinberg, Kiseleva, and Gel'fman (84) we have

$$Pd^{+2}(aq) + 4I^-(aq) = PdI_4^{-2}(aq) \qquad \log \beta_4 = 25$$

and calculate

$$Pd(c) + 4I^-(aq) = PdI_4^{-2}(aq) + 2e^- \qquad E° = -0.18 \text{ v}$$

This value is in good agreement with a reported (68) $E(1\ M\ KI) = -0.19$ v for the $Pd|PdI_4^{-2}$ couple.

The values we cite for $PdI_2(c)$ are based on high-temperature decomposition studies by Shchukarev, Tomacheva, and Pazukhina (179).

Thomsen (193) has reported $\Delta H = -22.6$ kcal for

$$PdCl_4^{-2}(aq) + 2I^-(aq) + H_2O(liq) = PdI_2 \cdot H_2O(c) + 4Cl^-(aq)$$

and Joannis (106) has reported $\Delta H = -18.4$ kcal for the analogous reaction of $PdBr_4^{-2}(aq)$. Combination of these results with previously cited heats leads to $\Delta H_f° = -83$ kcal mole^{-1} for $PdI_2 \cdot H_2O(c)$. Further combination of this $\Delta H_f°$ with an estimated $S°_{298} = (48)$ cal deg^{-1} mole^{-1} gives $\Delta G_f° = -70$ kcal mole^{-1} for $PdI_2 \cdot H_2O(c)$. This $\Delta G_f°$ yields a calculated $K_{sp} = 10^{-23}$. From the $\Delta G_f°$ for $PdI_2(c)$ already cited (179) we also calculate $K_{sp} = 10^{-23}$. It therefore appears possible that PdI_2 rather than the monohydrate was precipitated in the calorimetric experiments (106, 193). On this basis, we calculate $\Delta H_f° = -14$ kcal mole^{-1} for precipitated PdI_2, which is the same as the value already cited (179) for $PdI_2(c)$ on the basis of high-temperature data. The rejected $\Delta H_f°$ values for $PdCl_4^{-2}(aq)$ lead to inconsistent $\Delta H_f°$ values here unless we arbitrarily reject other results.

The old work of Isambert (103) leads to the heats of formation we tabulate for $Pd(NH_3)_2Cl_2(c)$, $Pd(NH_3)_4Cl_2(c)$, $Pd(NH_3)_2I_2(c)$, and $Pd(NH_3)_4I_2(c)$. Heats of formation of $PdBr_2(c)$ and $Pd(CN)_2(c)$ are from the old work of Joannis (106).

Wellman (204) has determined an equilibrium constant for oxidation of $PdCl_4^{-2}(aq)$ to $PdCl_6^{-2}(aq)$ by chlorine. From his results we calculate $\Delta G_f° = -103$ kcal mole^{-1} for $PdCl_6^{-2}(aq)$ and thence

$$PdCl_4^{-2}(aq) + 2Cl^-(aq) = PdCl_6^{-2}(aq) + 2e^- \quad E° = -1.26 \text{ v}$$

and

$$Pd(c) + 6Cl^-(aq) = PdCl_6^{-2}(aq) + 4e^- \qquad E° = -0.92 \text{ v}$$

The above value for the $PdCl_4^{-2}|PdCl_6^{-2}$ couple is in reasonable agreement with $E(1\ M\ HCl) = -1.29$ v, obtained by Grinberg and Shamsiev (91), who also report the following.

$$PdBr_4^{-2}(aq) + 2Br^-(aq) = PdBr_6^{-2}(aq) + 2e^- \qquad E(1\ M\ KBr) = -0.99 \text{ v}$$

$$PdI_4^{-2}(aq) + 2I^-(aq) = PdI_6^{-2}(aq) + 2e^- \qquad E(1\ M\ KI) = -0.48 \text{ v}$$

Combinations of these potentials with previously cited potentials lead to

$$Pd(c) + 6Br^-(aq) = PdBr_6^{-2}(aq) + 4e^- \qquad E° = -0.74 \text{ v}$$

and

$$Pd(c) + 6I^-(aq) = PdI_6^{-2}(aq) + 4e^- \qquad E° = -0.33 \text{ v}$$

Wellman (204) also determined the solubility of $K_2PdCl_6(c)$, from which we calculate its $\Delta G_f° \cong -246$ kcal mole^{-1}. Thomsen's calorimetric data (193) offer two aqueous paths to $\Delta H_f°$ of $K_2PdCl_6(c)$, the results averaging at ~ -290 kcal mole^{-1}. Puche (153) has studied the decomposition of $K_2PdCl_6(c)$ to $K_2PdCl_4(c)$ and $Cl_2(g)$. From his results we calculate $\Delta H_f° \cong -277$ kcal mole^{-1} for $K_2PdCl_6(c)$ and hesitantly cite this value in Table VI because it leads to a more reasonable entropy than does Thomsen's (193) $\Delta H_f°$.

From pH, spectrophotometric, and solubility measurements, Izatt, Eatough, and Christensen (104) have found the following.

$$Pd^{+2}(aq) + OH^-(aq) = Pd(OH)^+(aq) \qquad \log K = 12.7$$

$$Pd^{+2}(aq) + 2OH^-(aq) = Pd(OH)_2(aq) \qquad \log K = 26.1$$

$$Pd(OH)_2(c) = Pd(OH)_2(aq) \qquad \log K = -2.7$$

These last two equilibrium constants lead to $K_{sp} = 2 \times 10^{-29}$ and $\Delta G_f° = -72$ kcal mole^{-1} for $Pd(OH)_2(c)$. We calculate

$$Pd(c) + 2OH^-(aq) = Pd(OH)_2(c) + 2e^- \qquad E° = -0.07 \text{ v}$$

We have no electrochemical data for this potential, but Sawyer and Interrante (163) have reported a surface potential.

$$Pd(c) + 2OH^-(aq) = Pd(OH)_2(\text{surface}) + 2e^- \qquad E(0.1\ M\ K_2SO_4) = -0.19 \text{ v}$$

Calorimetric measurements by Thomsen (193) lead to $\Delta H = -12.6$ kcal for

$$PdCl_4^{-2}(aq) + 2OH^-(aq) = Pd(OH)_2(c) + 4Cl^-(aq)$$

Joannis (106) has reported $\Delta H = -9$ kcal for the corresponding reaction with $PdBr_4^{-2}(aq)$. These heats of reaction lead to $\Delta H_f° = -88$ kcal mole^{-1} for $Pd(OH)_2(c)$. Combination of this value with the $\Delta G_f°$ cited above yields $S°_{298} \cong 36$ cal deg^{-1} mole^{-1} for $Pd(OH)_2(c)$. Comparison of this value with more reliably known entropies of other $M(OH)_2$ compounds suggests that this calculated $S°_{298}$ is 10 to 15 cal deg^{-1} mole^{-1} too large, but it should be noted that a rejected (105) $\Delta H_f°$ value for $PdCl_4^{-2}(aq)$ would have led to

$S^\circ_{298} \cong 76$ cal deg^{-1} mole^{-1} for $Pd(OH)_2(c)$. This latter entropy is clearly too large to be acceptable. Unfortunately for the sake of a consistent representation of all the data, it should be noted that the rejected ΔH_f° from Thomsen (193) would lead to $S^\circ_{298} \cong 22$ cal deg^{-1} mole^{-1} for $Pd(OH)_2(c)$, which appears to be a reasonable value. A third-law entropy for $Pd(OH)_2(c)$ would be useful.

Thomsen (193) has measured the heat of reaction of $K_2PdCl_6(c)$ with $OH^-(aq)$ to form $Pd(OH)_4(c)$. His result permits us to calculate $\Delta H_f^\circ \cong -155$ kcal mole^{-1} for $Pd(OH)_4(c)$. Jirsa (105a) has reported $E^\circ = -0.95$ v for the $Pd(OH)_2|Pd(OH)_4$ couple. This value is more negative than seems reasonable on the basis of qualitative chemical evidence and in combination with already cited data for $Pd(OH)_2$ and the ΔH_f° given above leads to a *negative* entropy for $Pd(OH)_4(c)$. Rather than accept Jirsa's value, we estimate $S^\circ = (35)$ cal deg^{-1} mole^{-1} for $Pd(OH)_4(c)$ and combine with the above ΔH_f° to obtain ΔG_f° and thence the calculated potentials.

$$Pd(OH)_2(c) + 2OH^-(aq) = Pd(OH)_4(c) + 2e^- \quad E^\circ = -0.7 \text{ v}$$

$$Pd(c) + 4OH^-(aq) = Pd(OH)_4(c) + 4e^- \quad E^\circ = -0.4 \text{ v}$$

Fasman, Kutyukov, and Sokol'skii (68) have reported data that lead to $E(0.5\ M\ KCN) = 0.56$ v for the $Pd|Pd(CN)_4^{-2}$ couple and to $\log \beta_4 = 50$ for $Pd(CN)_4^{-2}(aq)$. The data of Izatt, Watt, Eatough, and Christensen (105) lead to $\log \beta_4$ for $Pd(CN)_4^{-2}(aq)$ and thence to $E^\circ = 0.33$ v for the $Pd|Pd(CN)_4^{-2}$ couple. These latter workers (105) have reported $\Delta H^\circ = -92$ kcal and $\Delta S^\circ = -116$ cal deg^{-1} for

$$Pd^{+2}(aq) + 4CN^-(aq) = Pd(CN)_4^{-2}(aq)$$

and have noted that this ΔS° is very much more negative than $\Delta S^\circ = -7$ for the corresponding reaction of $Ni^{+2}(aq)$. Combination of the larger (68) $\log \beta_4$ with the calorimetric (105) ΔH° leads to $\Delta S^\circ = -80$ for the $Pd(CN)_4^{-2}$ reaction, which is also much more negative than for the corresponding Ni^{+2} reaction. In view of these uncertainties, we tabulate no data for $Pd(CN)_4^{-2}(aq)$. The following approximate potential may be useful.

$$Pd(c) + 4CN^-(aq) = Pd(CN)_4^{-2}(aq) + 2e^- \quad E^\circ \cong 0.4 \text{ v}$$

From the results of several investigators (26, 68, 77, 84, 185) we select the following.

$$Pd(c) + 4SCN^-(aq) = Pd(SCN)_4^{-2}(aq) + 2e^- \quad E^\circ \cong -0.14 \text{ v}$$

$$Pd^{+2}(aq) + 4SCN^-(aq) = Pd(SCN)_4^{-2}(aq) \quad \log \beta_4 \cong 26$$

Fasman's emf measurements (68) lead to the following.

$$Pd(c) + 4NO_2^-(aq) = Pd(NO_2))_4^{-2}(aq) + 2e^- \quad E(0.5\ M\ KNO_2) = -0.34 \text{ v}$$

$$Pd^{+2}(aq) + 4NO_2^-(aq) = Pd(NO_2)_4^{-2}(aq) \quad \log \beta_4 \cong 20$$

Fasman (68) has reported results of emf measurements that ostensibly refer to the $Pd|Pd(NH_3)_4^{+2}$ couple, but the cell reaction is poorly defined and we are unable to calculate a meaningful standard potential. The best results appear to be from Grinberg, Kiseleva, and Gel'fman (85), who report $\log \beta_4 = 30.5$ ($\mu = 1.0$) for

$$Pd^{+2}(aq) + 4NH_3(aq) = Pd(NH_3)_4^{+2}(aq)$$

We calculate the potential

$$Pd(c) + 4NH_3(aq) = Pd(NH_3)_4^{+2}(aq) + 2e^- \quad E^\circ = 0.0 \text{ v}$$

Some related stability constants (156) have been determined and both solubility (155) and thermal (103) data are available for $Pd(NH_3)_2Cl_2(c)$.

Spectrophotometric measurements (181) give $K = 6 \times 10^{-10}$ for

$$PdCl_4^{-2}(aq) + 2N_3^-(aq) = Pd(N_3)_2Cl_2^{-2}(aq) + 2Cl^-(aq)$$

We now turn to some data for Pd(II) that cannot be related to free energies or potentials already cited. Fasman (68) has reported

$$Pd(c) + 4Thi(aq) = Pd(Thi)_4^{+2}(aq) + 2e^- \quad E(0.5\ M) = -0.07 \text{ v}$$

(Thi = thiourea)

Equilbrium constants for Pd(II) complex species involving thiourea with Cl^-, Br^-, and SCN^- have been reported (184).

Stability constants at 20 and 30° have been reported (59) for $Pd(Ch)_n^{2-n}(aq)$ ($n = 1$ and 2; Ch = acetylacetonate) and approximate ΔH values have been calculated.

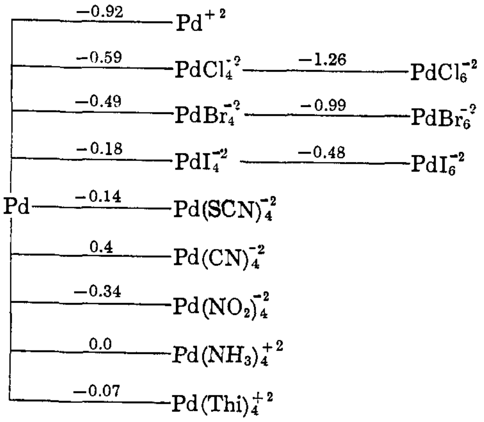
Conductance measurements (99) lead to $Q_{2,0} = 17$ for

$$PdCl_4^{-2} + C_2H_4(aq) = PdCl_3(C_2H_4)^-(aq) + Cl^-(aq)$$

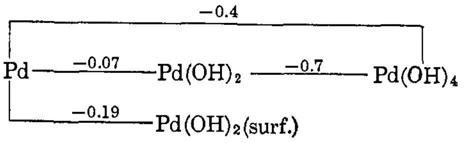
The solubility product of $Pd(DMG)_2(c)$ (DMG =

SCHEME V

ACIDIC OR NEUTRAL SOLUTION



BASIC SOLUTION



dimethylglyoxime) is reported (33) to be $\sim 10^{-34}$.

Babaeva and Khananova (7) have reported the following potentials for ethylenediamine complexes.

$$Pd(en)_2{}^{+2}(aq) + 2Cl^-(aq) = PdCl_2(en)_2{}^{+2}(aq) + 2e^- \qquad E° = -1.13 \text{ v}$$

$$Pd(en)_2{}^{+2}(aq) + 2Br^-(aq) = PdBr_2(en)_2{}^{+2}(aq) + 2e^- \qquad E° = -0.69 \text{ v}$$

$$Pd(en)_2{}^{+2}(aq) + 2I^-(aq) = PdI_2(en)_2{}^{+2}(aq) + 2e^- \qquad E° = -0.63 \text{ v}$$

Considerable information from the preceding pages is summarized in the potential diagrams of Scheme V.

VII. PLATINUM

A. DESCRIPTIVE CHEMISTRY

The chemistry of platinum involves a considerable variety of species that contain platinum in oxidation states ranging from 0 to +6. We begin with a summary of reactions of the element and then consider some compounds and aqueous species, progressing from higher to lower oxidation states.

Platinum reacts with oxygen at ~440° and 8 atm to form the monoxide, PtO. Reaction of the metal with fluorine at high temperature yields PtF_4, whereas reaction with chlorine yields $PtCl_2$. Although platinum is not attacked by hot nitric acid, it reacts readily with aqua regia to form chloroplatinic acid, H_2PtCl_6. The hexahydrate of chloroplatinic acid, $H_2PtCl_6 \cdot 6H_2O$, is obtained when the metal is treated with chlorine in hydrochloric acid. Platinum tetrabromide can be prepared by treating the metal with a mixture of bromine and hydrobromic acid. Hydrous K_2PtO_3 is obtained when the metal is heated with a melt of KOH and KNO_3, while a poorly characterized sulfate results when molten $KHSO_4$ is used. The adduct compound $PtF_4 \cdot 2BrF_3$ is obtained when platinum is treated with liquid BrF_3.

The trioxide PtO_3 is prepared by anodic oxidation of PtO_2(hyd) in KOH at 0°. It is an extremely unstable compound that easily loses oxygen. Reaction of platinum with fluorine in a silica vessel yields $PtOF_4$, while the hexafluoride is prepared by passing an electric current through a platinum filament in fluorine gas. This latter reaction is exothermic, but the product PtF_6 is the least stable of the known hexafluorides. It reacts with O_2 to form $O_2{}^+PtF_6{}^-$ and with Xe to form $Xe(PtF_6)_n$.

The potassium salt of $Pt^VF_6{}^-$ is prepared by treating $O_2{}^+PtF_6{}^-$ with KI in IF_7. Other examples of Pt(V) are the oxyfluoride $PtOF_3$ and $[PtF_5]_n$, the latter being prepared by heating $PtCl_2$ with fluorine at 350°.

Many compounds and ions contain platinum in the +4 oxidation state. As mentioned above, PtF_4 and $PtBr_4$ can be prepared by reactions of the metal. The tetrachloride $PtCl_4$ is obtained by the thermal decomposition of solid H_2PtCl_6 with KI. The tetrafluoride PtF_4 is decomposed in water. However, $PtCl_4$ is water soluble, and it has been suggested that the aqueous species should be formulated as $PtCl_4(OH)_2{}^{-2}$. The tetrabromide and tetraiodide are only sparingly soluble in water.

Ions of type $PtX_6{}^{-2}$ (X = Cl, Br, I, NO_2, CN, etc.) as well as a variety of mixed species are known both in aqueous solution and in salts. For example, all ammines from $[Pt(NH_3)_6]Cl_4$ to $K[PtCl_5NH_3]$, including stereoisomers, are known. The disulfide PtS_2 is obtained when $PtCl_6{}^{-2}(aq)$ is treated with H_2S. When $PtCl_6{}^{-2}(aq)$ is boiled with NaOH, PtO_2 (hyd) is obtained. The freshly precipitated hydrous oxide dissolves in either acid or base.

The trihalides $PtCl_3$, $PtBr_3$, and PtI_3 can be prepared by the thermal decomposition of the respective tetrahalides. All of these trihalides disproportionate in water. The oxide Pt_2O_3 is poorly characterized and may be $PtO \cdot PtO_2$.

The dihalides $PtCl_2$, $PtBr_2$, and PtI_2 can all be prepared by thermal decomposition of the higher halides. When $PtCl_2$ is dissolved in aqueous HCl, the anion $PtCl_4{}^{-2}$ is formed along with some $PtCl_6{}^{-2}$ and metallic platinum. A great variety of ions of type $PtX_4{}^{-2}$ (X = Cl, Br, I, NO_2, CN, etc.) and $Pt(NH_3)_4{}^{+2}$ as well as mixed forms are known. The sulfide PtS is precipitated when H_2S is passed through $PtCl_4{}^{-2}(aq)$.

Platinum in the +1 oxidation state is known only at high temperatures in the form of PtCl, PtBr, and perhaps PtI.

Platinum in the zero oxidation state in the form of $Pt(NH_3)_4$ can be obtained by treating $Pt(NH_3)_4{}^{+2}$ with potassium in liquid ammonia. The yellow-white compound readily decomposes to platinum and ammonia. Other compounds containing Pt(0) are $Pt(PAr_3)_4$ (Ar = aryl) and $Pt(en)_2$.

B. THERMOCHEMISTRY

We now turn to detailed consideration of the thermodynamic properties of platinum and its compounds. For Pt(c) and Pt(g) we adopt the entropies tabulated by Kelley and King (112). Two independent investigations (57, 96) are in good agreement with $\Delta H°_{298} = 135$ kcal mole^{-1} for sublimation of platinum. We combine this $\Delta H°$ with the entropies to obtain $\Delta G_f°$ for Pt(g).

Thermochemical data for the oxides of platinum are scarce. Novak and Markovic (139) have reviewed the numerous (unsuccessful) attempts to obtain stable Pt|Pt oxide electrodes and present what they believe to be the best approximate potentials. Thomsen (193) has measured the heat of reaction of $Pt(OH)_2(c)$ with HCOOH(aq) to form Pt(c), $CO_2(g)$, and water. From his data we calculate $\Delta H_f° = -84$ kcal mole^{-1} for $Pt(OH)_2(c)$. We estimate the entropy of $Pt(OH)_2(c)$

to be (30) cal deg^{-1} mole^{-1} and calculate $\Delta G_f^\circ \cong -66$ kcal mole^{-1} and thence

$$\mathrm{Pt(c) + 2OH^-(aq) = Pt(OH)_2(c) + 2e^-} \qquad E^\circ = -0.2\ \mathrm{v}$$

We have no direct measurement of the above potential. However, Sawyer and Interrante (163) have reported the surface potential

$$\mathrm{Pt(c) + 2OH^-(aq) = Pt(OH)_2(surface) + 2e^-} \qquad E(0.1\ M\ \mathrm{K_2SO_4}) = -0.14\ \mathrm{v}$$

We are also able to cite thermochemical data for PtO_2(g), whose decomposition at high temperature has been studied (1, 166), and Pt_3O_4(c), whose approximate heat of formation was determined (5) by reduction by hydrogen and high-temperature decomposition.

Third-law entropies have been determined (92, 205) for PtS(c) and PtS_2(c). These same workers (92, 205) have reinterpreted the decomposition data obtained by Biltz and Juza (22) to obtain ΔG_f° and ΔH_f° values for PtS(c) and PtS_2(c).

Third-law entropies are also known (92, 205) for PtTe(c) and $PtTe_2$(c).

A calculated (202) entropy for PtF_6(g) combined with vapor pressure data (203) leads to $S^\circ_{298} = 58$ cal deg^{-1} mole^{-1} for PtF_6(c, cubic).

Cell data (80, 211) for the Pt|$PtCl_4^{-2}$ couple are in good agreement, and we write

$$\mathrm{Pt(c) + 4Cl^-(aq) = PtCl_4^{-2}(aq) + 2e^-} \qquad E^\circ = -0.75\ \mathrm{v}$$

The $PtCl_4^{-2}$|$PtCl_6^{-2}$ couple has been investigated by several workers (87, 128, 188, 210), and we adopt the average of their results.

$$\mathrm{PtCl_4^{-2}(aq) + 2Cl^-(aq) = PtCl_6^{-2}(aq) + 2e^-} \qquad E^\circ = -0.77\ (\pm 0.05)\ \mathrm{v}$$

Combination of the potentials above leads to

$$\mathrm{Pt(c) + 6Cl^-(aq) = PtCl_6^{-2}(aq) + 4e^-} \qquad E^\circ = -0.76\ \mathrm{v}$$

From these potential data we calculate $\Delta G_f^\circ = -91$ kcal mole^{-1} for $PtCl_4^{-2}$(aq) and $\Delta G_f^\circ = -118$ kcal mole^{-1} for $PtCl_6^{-2}$(aq).

A third-law entropy (49) for K_2PtCl_6(c) combined with its solubility (4) and heat of solution (49) leads to $\bar{S}_2^\circ = 53$ cal deg^{-1} mole^{-1} for $PtCl_6^{-2}$(aq). Combination of this entropy with the already determined ΔG_f° leads to $\Delta H_f^\circ = -162$ kcal mole^{-1} for $PtCl_6^{-2}$(aq). The calorimetric heat of reduction of $PtCl_6^{-2}$(aq) to Pt(c) by Co(c) offers an alternative path to the ΔH_f° of $PtCl_6^{-2}$(aq), and measurements of this quantity by nineteenth century thermochemists (147, 193) lead to ΔH_f° values ranging from -161 to -163 kcal mole^{-1}.

There are several paths to the ΔH_f° of $PtCl_4^{-2}$(aq) and thence its partial molal entropy. Calorimetric measurements by Thomsen(193) lead *via* two alternate paths to $\Delta H_f^\circ = -116$ and -121 kcal mole^{-1}. A measurement (29) of the heat of reduction of $PtCl_4^{-2}$(aq) to Pt(c) by H_2(g) leads to $\Delta H_f^\circ = -119$ kcal mole^{-1}, while the change in potential of the Pt|$PtCl_4^{-2}$ couple with temperature (211) leads to $\Delta H_f^\circ = -133$ kcal mole^{-1}. Other workers (128, 210) have determined dE°/dT for the $PtCl_4^{-2}$|$PtCl_6^{-2}$ couple. Their results lead to values of $\Delta H_f^\circ = -104$ and -109 kcal mole^{-1} for $PtCl_4^{-2}$(aq). The ΔH_f° values above combined with ΔG_f° lead to $\bar{S}_2^\circ = 64, 48, 54, 8, 104,$ and 87 cal deg^{-1} mole^{-1} for $PtCl_4^{-2}$(aq). Since we are unable to make a completely objective choice between these conflicting data, the best we are able to do is to arbitrarily adopt "reasonable" values of $\bar{S}_2^\circ = (44)$ cal deg^{-1} mole^{-1} and $\Delta H_f^\circ = -122$ kcal mole^{-1} for $PtCl_4^{-2}$(aq). These values have been chosen in an effort to maintain consistency between data for $PtCl_4^{-2}$(aq) and what appear to be the "best" data for related compounds.

Cell measurements (80) lead to $E^\circ(18^\circ) \cong -0.67$ v for the Pt|$PtBr_4^{-2}$ couple, while reported (60) stability constants can be used to relate the ΔG_f°(aq) of $PtCl_4^{-2}$ to that of $PtBr_4^{2-}$(aq) and thence also to

$$\mathrm{Pt(c) + 4Br^-(aq) = PtBr_4^{-2}(aq) + 2e^-} \qquad E^\circ = -0.67\ \mathrm{v}$$

Thomsen's heat of reduction of $PtBr_4^{-2}$(aq) by Co(c) permits us to calculate $\Delta H_f^\circ = -89$ kcal mole^{-1} for $PtBr_4^{-2}$(aq). Combination with the ΔG_f° yields $\bar{S}_2^\circ \cong 47$ cal deg^{-1} mole^{-1} for $PtBr_4^{-2}$(aq).

An equilibrium study (149) allows us to relate the ΔG_f° of $PtBr_6^{-2}$(aq) to that of $PtCl_6^{-2}$(aq) and thus to calculate $E^\circ \cong -0.79$ v for the $PtBr_4^{-2}$|$PtBr_6^{-2}$ couple. We believe cell measurements (89) on this couple to be more reliable and we adopt

$$\mathrm{PtBr_4^{-2}(aq) + 2Br^-(aq) = PtBr_6^{-2}(aq) + 2e^-} \qquad E(1\ M\ \mathrm{NaBr}) = -0.64\ \mathrm{v}$$

Combination of the above with the Pt|$PtBr_4^{-2}$ potential leads to

$$\mathrm{Pt(c) + 6Br^-(aq) = PtBr_6^{-2}(aq) + 4e^-} \qquad E^\circ = -0.66\ \mathrm{v}$$

Thomsen's (193) calorimetric measurements offer two paths to the ΔH_f° of $PtBr_6^{-2}$(aq) that are in good agreement. We adopt $\Delta H_f^\circ = -114$ kcal mole^{-1} and combine with ΔG_f° to calculate $\bar{S}_2^\circ = 67$ cal deg^{-1} mole^{-1} for $PtBr_6^{-2}$(aq).

From direct electrochemical measurements (80, 89) we obtain

$$\mathrm{Pt(c) + 4I^-(aq) = PtI_4^{-2}(aq) + 2e^-} \qquad E^\circ(18^\circ) \cong -0.40\ \mathrm{v}$$

and

$$\mathrm{PtI_4^{-2}(aq) + 2I^-(aq) = PtI_6^{-2}(aq) + 2e^-} \qquad E(1\ M\ \mathrm{NaI}) = -0.39\ \mathrm{v}$$

Combination of the above two potentials leads to

$$\mathrm{Pt(c) + 6I^-(aq) = PtI_6^{-2}(aq) + 4e^-} \qquad E^\circ \cong -0.40\ \mathrm{v}$$

The heat of reduction (147) of PtI_6^{-2}(aq) by Co(c) leads to $\Delta H_f^\circ = -50$ kcal mole^{-1} for PtI_6^{-2}(aq), and thence $\bar{S}_2^\circ \cong 81$ cal deg^{-1} mole^{-1}. We have no experimental data that lead to the heat and entropy for PtI_4^{-2}(aq), but we estimate the entropy to be (52)

TABLE VII

THERMODYNAMIC DATA FOR PLATINUM AT 298°K[a]

Substance	$\Delta H_f°$, kcal mole^{-1}	$\Delta G_f°$, kcal mole^{-1}	$S°$, cal deg^{-1} mole^{-1}
Pt(c)	0	0	9.95[112]
Pt(g)	135[57,96]	124	45.96[112]
Pt^{+2}(aq)		(57)	
$Pt(OH)_2$(c)	−84[193]	~−66	(30)
$Pt(OH)_2$(surf.)		−69[163]	
PtO_2(g)	41[166]	40[166]	62[166]
Pt_3O_4(c)	~−38[5]		
PtS(c)	−20[22,92]	−18[22,92]	13.2[92]
PtS_2(c)	−26[22,205]	−24[22,205]	17.9[205]
PtTe(c)			19.4[93]
$PtTe_2$(c)			28.9[205]
PtF_5(c, cubic)			58[203]
PtF_6(g)			83.2[202]
PtCl(c)	~−12[176]	~−9[175]	~27[176]
$PtCl_2$(c)	~−33[176]	~−23[176]	~28[176]
$PtCl_3$(c)	~−48[176]	~−32[176]	~36[176]
$PtCl_4$(c)	~−63[176]	~−41[176]	~42[176]
$PtCl_4 \cdot 5H_2O$(c)	~−426[147,176]		
$PtCl_4^{-2}$(aq)	−122	−91[80,211]	(44)
$PtCl_6^{-2}$(aq)	−162[147,193]	−118[87,128,188,210]	53[4,49]
PtBr(c)	~−7[178]	~−7[178]	~28[178]
$PtBr_2$(c)	~−15[178]	~−14[178]	~44[178]
$PtBr_3$(c)	~−23[178]	~−20[178]	~56[178]
$PtBr_4$(c)	~−29[178]	~−25[178]	~68[178]
$PtBr_4^{-2}$(aq)	−89[193]	−69[60,80]	~47
$PtBr_6^{-2}$(aq)	−114[193]	−89[89]	~67
PtI_4(c)	−16[147]		
PtI_4^{-2}(aq)	−44	−31[80]	(52)
PtI_6^{-2}(aq)	−50[147]	−37[89]	~81
$H_2PtCl_6 \cdot 6H_2O$(c)	−568[147]		
$H_2PtCl_5(OH) \cdot H_2O$(c)	−244[147]		
Na_2PtCl_6(c)	−269[72,193]		
$Na_2PtCl_6 \cdot 6H_2O$(c)	−697[193]		
Na_2PtBr_6(c)	−219[193]		
$Na_2PtBr_6 \cdot 6H_2O$(c)	−647[193]		
K_2PtCl_4(c)	−255[143,193]		
K_2PtCl_6(c)	−296[49,193]	−260[49]	79.8[49]
K_2PtBr_4(c)	−220[193]		
K_2PtBr_6(c)	−247[193]		
Rb_2PtCl_4(c)	−255[143]		
Cs_2PtCl_4(c)	−255[143]		
$BaPtCl_6$(c)	−282[72]		
$BaPtCl_6 \cdot 6H_2O$(c)	−702[72]		
$(NH_4)_2PtCl_4$(c)	−194[143]		
$(NH_4)_2PtCl_6$(c)	−237[182]		
Ag_2PtCl_6(c)	−126[147]		
Ag_2PtBr_6(c)	−96[147]		
$[Pt(NH_3)_4](NO_3)_2$(c)	−204[41]		
$[Pt(NH_3)_4]Cl_2$(c)	−177.5[42]		
$[Pt(NH_3)_4]Cl_2 \cdot H_2O$(c)	−248[193]		
$[Pt(NH_3)_4]I_2$(c)	−132[41]		
$Pt(NH_3)_4^{+2}$	−91[41]	−14[81]	~0
$Pt(NH_3)_3Cl^{+}$(aq)	−98[40]	~−26[83]	~−11(?)
$[Pt(NH_3)_3Cl]Cl$(c)	−148[42]		
$[Pt(NH_3)_3Cl]Br$(c)	−138[143]		
$[Pt(NH_3)_3Cl]ClO_4$(c)	−142[143]		
$[Pt(NH_3)_3Cl]_2[PtCl_4]$(c)	−353[43]		
$[Pt(NH_3)_3Cl][PtNH_3Cl_3]$(c)	−231[43]		
$[Pt(NH_3)_4][PtNH_3Cl_3]_2$(c)	−349[43]		
cis-$Pt(NH_3)_2Cl_2$(c)	−115[43]		
trans-$Pt(NH_3)_2Cl_2$(c)	−118[43]		
cis-$Pt(NH_3)_2Cl_2$(aq)		~−53[82]	
trans-$Pt(NH_3)_2Cl_2$(aq)		~−51[82]	
$PtNH_3Cl_3^{-}$(aq)	−115[40]	~−72[83]	−31
$K(PtNH_3Cl_3)$(c)	−185[40]		
$Rb[PtNH_3Cl_3]$(c)	−184[143]		
$Cs[PtNH_3Cl_3]$(c)	−185[143]		
$NH_4[PtNH_3Cl_3]$(c)	−153[43]		
cis-$Pt(NH_3)_2Cl_4$(aq)		~−84[86]	
trans-$Pt(NH_3)_2Cl_4$(aq)		~−82[86]	
cis-$Pt(NH_3)_2I_2$(aq)		~−24[82]	
trans-$Pt(NH_3)_2I_2$(aq)		~−22[82]	
$Pt(NH_3)_4Cl_2^{+2}$(aq)		−49[88]	
$Pt(NH_3)_4Br_2^{+2}$(aq)		−37[88]	
$Pt(NH_3)_4I_2^{+2}$(aq)		−19[88]	
$Pt(NH_3)_4(SCN)_2^{+2}$(aq)		53[125]	
$Pt(CN)_4^{-2}$(aq)		~169[80]	
$Pt(CN)_4Cl_2^{-2}$(aq)		~147[192]	
cis-$Pt(CH_3NH_2)_2Cl_2$(aq)		~−28.7[82]	
trans-$Pt(CH_3NH_2)_2Cl_2$(aq)		~−29.2[82]	
cis-$Pt(CH_3NH_2)_2I_2$(aq)		~−1[82]	
trans-$Pt(CH_3NH_2)_2I_2$(aq)		~1[82]	
$Pt(CH_3NH_2)_4^{+2}$(aq)		~29[81]	
$PtNH_3Cl_5^{-}$(aq)		~−102[87]	
$Pt(NH_3)_3Cl_3^{+}$(aq)		~−59[87]	
cis-$Pt(NH_3)_2I_4$(aq)		~−31[88]	
trans-$Pt(NH_3)_2I_4$(aq)		~−29[88]	

[a] Superscript numbers are references.

cal deg^{-1} mole^{-1} and calculate $\Delta H_f° \cong -44$ kcal mole^{-1}.

Heats of solution are known for many salts of platinum. We have used these heats of solution together with the $\Delta H_f°$ values already cited to calculate the heats of formation (references cited in Table VII) of the following compounds: $H_2PtCl_5(OH) \cdot H_2O$(c), $H_2PtCl_6 \cdot 6H_2O$(c), Na_2PtCl_6(c), $Na_2PtCl_6 \cdot 6H_2O$(c), Na_2PtBr_6(c), $Na_2PtBr_6 \cdot 6H_2O$(c), K_2PtCl_4(c), K_2PtCl_6(c), K_2PtBr_4(c), K_2PtBr_6(c), Rb_2PtCl_4(c), Cs_2PtCl_4(c), $BaPtCl_6$(c), $BaPtCl_6 \cdot 6H_2O$(c), $(NH_4)_2PtCl_4$(c), and $(NH_4)_2PtCl_6$(c).

The values we cite for the chlorides and bromides of platinum are based on the high-temperature equilibrium work of Russian workers (176, 178), who were careful to demonstrate in each case the homogeneity of the solid phase by means of X-ray analysis. In the absence of heat content data we have estimated $\Delta C_p°$ in interpreting their (176, 178) results.

Old calorimetric measurements (147) lead by two different paths to −57 and −58 kcal mole^{-1} for $\Delta H_f°$ of $PtCl_4$(c). For the sake of consistency with the lower chlorides we adopt the heat based on the high-temperature decomposition work (176), but it should be noted that a value of $\Delta H_f° = -57.5$ kcal mole^{-1} for $PtCl_4$(c) may in fact be closer to the truth than the value we adopt. The heat of formation of $PtCl_4 \cdot 5H_2O$(c) is based upon the calorimetric measurements of Pigeon (147) and the $\Delta H_f°$ for $PtCl_4$(c) cited in Table VII.

Calorimetric measurements (147) lead by two different paths to $\Delta H_f° = -38$ and -40 kcal mole^{-1} for $PtBr_4$(c). Again we rather arbitrarily adopt $\Delta H_f° \cong -29$ kcal mole^{-1} from the high-temperature decomposition study (178).

The heats of reaction of Ag^{+}(aq) with $PtCl_6^{-2}$(aq) and $PtBr_6^{-2}$(aq) to form Ag_2PtCl_6(c) and Ag_2PtBr_6(c) have been measured (147), leading to the tabulated $\Delta H_f°$ values.

The heat of formation of PtI_4(c) cited in Table VII is based on a calorimetric measurement (147). A high-temperature decomposition study of the platinum iodides has been attempted (180), and it was reported that PtI(c) may exist at high temperatures.

Chernyaev, Palkin, and Baranova (42) have measured the heats of reaction of K_2PtCl_4(c) and $(NH_4)_2PtCl_4$(c) with NH_3(g), permitting us to calculate $\Delta H_f^\circ = -177.5$ kcal mole^{-1} for the product $[Pt(NH_3)_4]Cl_2$(c). This compound is also the final product in the reactions of ammonia with $NH_4[PtNH_3Cl_3]$(c), *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$(c), $[Pt(NH_3)_3Cl][PtNH_3Cl_3]$, $[Pt(NH_3)_3Cl]_2[PtCl_4]$(c), $[Pt(NH_3)_4][PtNH_3Cl_3]_2$(c), and $[Pt(NH_3)_3Cl]Cl$(c). We have used the calorimetric (42, 43) heats of these reactions in calculating the heats of formation of the above-mentioned compounds.

Chernyaev and Palkin (40, 192) report heats of solution for $[Pt(NH_3)_4]Cl_2$(c), $NH_4[PtNH_3Cl_3]$(c), and $[Pt(NH_3)_3Cl]Cl$(c), thus allowing us to calculate heats of formation for $[Pt(NH_3)_4]^{+2}$(aq), $[PtNH_3Cl_3]^-$(aq), and $[Pt(NH_3)_3Cl]^+$(aq). Other (40, 41, 143, 193) heats of solution are used to calculate heats of formation for $K[PtNH_3Cl_3]$(c), $Rb[PtNH_3Cl_3]$(c), $Cs[PtNH_3Cl_3]$(c), $[Pt(NH_3)_3Cl]Br$(c), $[Pt(NH_3)_3Cl]ClO_4$(c), $[Pt(NH_3)_4]Cl_2\cdot H_2O$(c), $[Pt(NH_3)_4]I_2$(c), and $[Pt(NH_3)_4](NO_3)_2$(c).

From the emf data of Grinberg and Gel'fman (80) we obtain

$$Pt(c) + 4CN^-(aq) = Pt(CN)_4^{-2}(aq) + 2e^- \qquad E^\circ(18^\circ) \cong -0.09 \text{ v}$$

and from Terrey (192) we have

$$Pt(CN)_4^{-2}(aq) + 2Cl^-(aq) = Pt(CN)_4Cl_2^{-2}(aq) + 2e^- \qquad E^\circ(13^\circ) = -0.89 \text{ v}$$

The approximate free energies we cite for $Pt(CN)_4^{-2}$(aq) and $Pt(CN)_4Cl_2^{-2}$(aq) are calculated from the above potentials.

From the emf data obtained by Grinberg and Gel'fman (81) we obtain

$$Pt(c) + 4NH_3(aq) = Pt(NH_3)_4^{+2}(aq) + 2e^- \qquad E(0.092\ M\ NH_3, 18^\circ) = -0.25 \text{ v}$$

Combination with the previously cited heat of formation leads to $\bar{S}_2^\circ \cong 0$ cal deg^{-1} mole^{-1} for $Pt(NH_3)_4^{+2}$(aq). These same workers (83) present emf data that lead to the approximate potentials

$$Pt(c) + NH_3(aq) + 3Cl^-(aq) = PtNH_3Cl_3^-(aq) + 2e^- \qquad E(1\ M, 18^\circ) \cong -0.61 \text{ v}$$

and

$$Pt(c) + 3NH_3(aq) + Cl^-(aq) = Pt(NH_3)_3Cl^+(aq) + 2e^- \qquad E(1\ M, 18^\circ) \cong -0.54 \text{ v}$$

Combination with the already cited ΔH_f° values leads to $\bar{S}_2^\circ \cong 31$ cal deg^{-1} mole^{-1} for $PtNH_3Cl_3^-$(aq) and $\bar{S}_2^\circ \cong -11$ cal deg^{-1} mole^{-1} for $Pt(NH_3)_3Cl^+$(aq). This latter entropy appears to be much too low and we tabulate it with a question mark.

Grinberg, Lavrent'ev, and Ptitsyn (87) have reported the following potentials.

$$PtNH_3Cl_3^-(aq) + 2Cl^-(aq) = PtNH_3Cl_5^-(aq) + 2e^- \qquad E^\circ = -0.70 \text{ v}$$

$$Pt(NH_3)_3Cl^+(aq) + 2Cl^-(aq) = Pt(NH_3)_3Cl_3^+(aq) + 2e^- \qquad E^\circ = -0.64 \text{ v}$$

Combinations of potentials above lead to the following.

$$Pt(c) + NH_3(aq) + 5Cl^-(aq) = PtNH_3Cl_5^-(aq) + 4e^- \qquad E^\circ \cong -0.66 \text{ v}$$

$$Pt(c) + 3NH_3(aq) + 3Cl^-(aq) = Pt(NH_3)_3Cl_3^+(aq) + 4e^- \qquad E^\circ \cong -0.59 \text{ v}$$

From other emf measurements (87, 88) we obtain

$$Pt(NH_3)_4^{+2}(aq) + 2Cl^-(aq) = Pt(NH_3)_4Cl_2^{+2}(aq) + 2e^- \qquad E^\circ = -0.60 \text{ v}$$

$$Pt(NH_3)_4^{+2}(aq) + 2Br^-(aq) = Pt(NH_3)_4Br_2^{+2}(aq) + 2e^- \qquad E(10^{-4}\ M) = -0.58 \text{ v}$$

$$Pt(NH_3)_4^{+2}(aq) + 2I^-(aq) = Pt(NH_3)_4I_2^{+2}(aq) + 2e^- \qquad E(2 \times 10^{-4}\ M) = -0.43 \text{ v}$$

Rettew and Johnson (159) report

$$trans\text{-}Pt(NH_3)_4Cl_2^{+2}(aq) + 2Br^-(aq) = trans\text{-}Pt(NH_3)_4Br_2^{+2}(aq) + 2Cl^-(aq) \qquad \log Q(0.2\ M) = 1.85$$

Appropriate manipulation of potentials given above leads to $\log K = 0.7$ for this equilibrium, although it should be noted that the workers who measured the potentials did *not* specify if the relevant species were *cis* or *trans*.

Mason, Berger, and Johnson (125) report

$$trans\text{-}Pt(NH_3)_4Cl_2^{+2}(aq) + 2SCN^-(aq) = trans\text{-}Pt(NH_3)_4(SCN)_2^{+2}(aq) + 2Cl^-(aq) \qquad \log K(35^\circ) = 3.6$$

From this datum we calculate (not specifying the *cis* or *trans* nature of the species)

$$Pt(NH_3)_4^{+2}(aq) + 2SCN^-(aq) = Pt(NH_3)_4(SCN)_2^{+2}(aq) + 2e^- \qquad E^\circ \cong -0.49 \text{ v}$$

From the work of Grinberg and Gel'fman (82) we obtain

$$Pt(c) + 2NH_3(aq) + 2Cl^-(aq) = cis\text{-}Pt(NH_3)_2Cl_2(aq) + 2e^- \qquad E(1\ M, 18^\circ) \cong -0.49 \text{ v}$$

and

$$Pt(c) + 2NH_3(aq) + 2Cl^-(aq) = trans\text{-}Pt(NH_3)_2Cl_2(aq) + 2e^- \qquad E(1\ M, 18^\circ) \cong -0.53 \text{ v}$$

Grinberg and Lavrent'ev (86) also report

$$cis\text{-}Pt(NH_3)_2Cl_2(aq) + 2Cl^-(aq) = cis\text{-}Pt(NH_3)_2Cl_4(aq) + 2e^- \qquad E(1\ M\ NaCl) = -0.69 \text{ v}$$

and

$$trans\text{-}Pt(NH_3)_2Cl_2(aq) + 2Cl^-(aq) = trans\text{-}Pt(NH_3)_2Cl_4(aq) + 2e^- \qquad E(1\ M\ NaCl) = -0.69 \text{ v}$$

By combination of the above couples we calculate

$$Pt(c) + 2NH_3(aq) + 4Cl^-(aq) = cis\text{-}Pt(NH_3)_2Cl_4(aq) + 4e^- \qquad E^\circ \cong -0.59 \text{ v}$$

and

$$Pt(c) + 2NH_3(aq) + 4Cl^-(aq) = trans\text{-}Pt(NH_3)_2Cl_4(aq) + 4e^- \qquad E^\circ \cong -0.61 \text{ v}$$

We also obtain the following approximate potentials for *cis* and *trans* species from the work of Grinberg and Gel'fman (82).

$$\mathrm{Pt(c) + 2NH_3(aq) + 2I^-(aq) = \mathit{cis}\text{-}Pt(NH_3)_2I_2(aq) + 2e^-} \qquad E(1\ M,\ 18°) \cong -0.29\ \mathrm{v}$$

$$\mathrm{Pt(c) + 2NH_3(aq) + 2I^-(aq) = \mathit{trans}\text{-}Pt(NH_3)_2I_2(aq) + 2e^-} \qquad E(1\ M,\ 18°) \cong -0.34\ \mathrm{v}$$

$$\mathrm{Pt(c) + 2CH_3NH_2(aq) + 2Cl^-(aq) = \mathit{cis}\text{-}Pt(CH_3NH_2)_2Cl_2(aq) + 2e^-} \qquad E(1\ M,\ 18°) \cong -0.52\ \mathrm{v}$$

$$\mathrm{Pt(c) + 2CH_3NH_2(aq) + 2Cl^-(aq) = \mathit{trans}\text{-}Pt(CH_3NH_2)_2Cl_2(aq) + 2e^-} \qquad E(1\ M,\ 18°) \cong -0.51\ \mathrm{v}$$

$$\mathrm{Pt(c) + 2CH_3NH_2(aq) + 2I^-(aq) = \mathit{cis}\text{-}Pt(CH_3NH_2)_2I_2(aq) + 2e^-} \qquad E(1\ M,\ 18°) \cong -0.29\ \mathrm{v}$$

$$\mathrm{Pt(c) + 2CH_3NH_2(aq) + 2I^-(aq) = \mathit{trans}\text{-}Pt(CH_3NH_2)_2I_2(aq) + 2e^-} \qquad E(1\ M,\ 18°) \cong -0.34\ \mathrm{v}$$

Grinberg and Orlova (88) report

$$\mathrm{\mathit{cis}\text{-}Pt(NH_3)_2I_2(aq) + 2I^-(aq) = \mathit{cis}\text{-}Pt(NH_3)_2I_4(aq) + 2e^-} \qquad E(2 \times 10^{-4}\ M) = -0.39\ \mathrm{v}$$

and

$$\mathrm{\mathit{trans}\text{-}Pt(NH_3)_2I_2(aq) + 2I^-(aq) = \mathit{trans}\text{-}Pt(NH_3)_2I_4(aq) + 2e^-} \qquad E(10^{-4}\ M) = -0.38\ \mathrm{v}$$

Combination with previously discussed couples leads to the following.

$$\mathrm{Pt(c) + 2NH_3(aq) + 4I^-(aq) = \mathit{cis}\text{-}Pt(NH_3)_2I_4(aq) + 4e^-} \qquad E° \cong -0.34\ \mathrm{v}$$

$$\mathrm{Pt(c) + 2NH_3(aq) + 4I^-(aq) = \mathit{trans}\text{-}Pt(NH_3)_2I_4(aq) + 4e^-} \qquad E° \cong -0.36\ \mathrm{v}$$

We calculate an approximate $\Delta G_f°$ for $\mathrm{Pt(CH_3NH_2)_4^{+2}(aq)}$ from the potential (81)

$$\mathrm{Pt(c) + 4CH_3NH_2(aq) = Pt(CH_3NH_2)_4^{+2}(aq) + 2e^-} \qquad E(0.0145\ M\ \mathrm{CH_3NH_2}) \cong -0.20\ \mathrm{v}$$

We have no experimental data that lead to $\Delta G_f°$ for $\mathrm{Pt^{+2}(aq)}$ and thence a value for the $\mathrm{Pt|Pt^{+2}}$ couple. Latimer (118) has estimated the K_{sp} of $\mathrm{Pt(OH)_2}$ to be $\sim 10^{-35}$, which leads to

$$\mathrm{Pt(c) = Pt^{2}(aq) + 2e^-} \qquad E° = (-1.2\ \mathrm{v})$$

This estimate then leads to $\log \beta_4 \cong 16$ for $\mathrm{PtCl_4^{-2}(aq)}$. Several workers (66, 90, 161) have reported instability constants for the ions $\mathrm{PtCl_n^{+2-n}}$ (n = 3 and 4), and the general trend of their results indicates that a value of $\log \beta_4 \cong 16$ is reasonable.

We conclude the section on platinum with a summary of some potential and equilibrium data that we believe to be of relevance to aqueous thermochemistry.

From the emf experiments of Grinberg and Orlova (88) we find

$$\mathrm{\mathit{cis}\text{-}Pt(NH_3)_2Br_2(aq) + 2Br^-(aq) = \mathit{cis}\text{-}Pt(NH_3)_2Br_4(aq) + 2e^-} \qquad E(2 \times 10^{-4}\ M) = -0.60\ \mathrm{v}$$

and

$$\mathrm{\mathit{trans}\text{-}Pt(NH_3)_2Br_2(aq) + 2Br^-(aq) = \mathit{trans}\text{-}Pt(NH_3)_2Br_4(aq) + 2e^-} \qquad E(3.3 \times 10^{-4}\ M) = -0.60\ \mathrm{v}$$

We summarize (86) some other Pt(II)|Pt(IV) couples (e = ethylamine, en = ethylenediamine, and gl = glycine).

$$\mathrm{\mathit{cis}\text{-}Pt(e)_2Cl_2(aq) + 2Cl^-(aq) = \mathit{cis}\ Pt(e)_2Cl_4(aq) + 2e^-} \qquad E(1\ M\ \mathrm{NaCl}) = -0.70\ \mathrm{v}$$

$$\mathrm{\mathit{trans}\text{-}Pt(e)_2Cl_2(aq) + 2Cl^-(aq) = \mathit{trans}\text{-}Pt(e)_2Cl_4(aq) + 2e^-} \qquad E(1\ M\ \mathrm{NaCl}) = -0.66\ \mathrm{v}$$

$$\mathrm{\mathit{cis}\text{-}Pt(gl)_2(aq) + 2Cl^-(aq) = \mathit{cis}\text{-}Pt(gl)_2Cl_2(aq) + 2e^-} \qquad E(1\ M\ \mathrm{NaCl}) = -0.64\ \mathrm{v}$$

$$\mathrm{\mathit{trans}\text{-}Pt(gl)_2(aq) + 2Cl^-(aq) = \mathit{trans}\text{-}Pt(gl)_2Cl_2(aq) + 2e^-} \qquad E(1\ M\ \mathrm{NaCl}) = -0.63\ \mathrm{v}$$

$$\mathrm{Pt(en)Cl_2(aq) + 2Cl^-(aq) = Pt(en)Cl_4(aq) + 2e^-} \qquad E(1\ M\ \mathrm{NaCl}) = -0.66\ \mathrm{v}$$

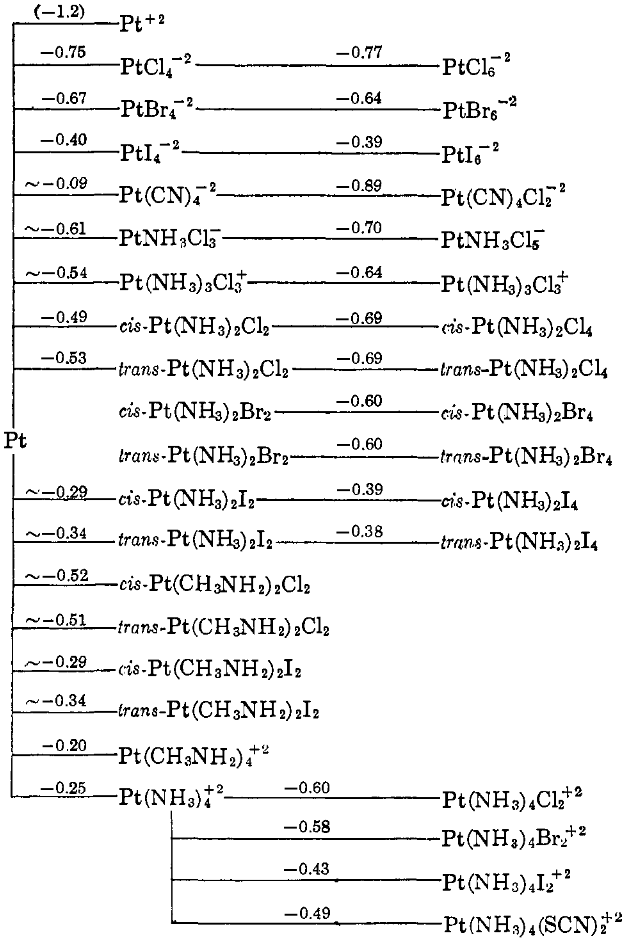
Grinberg, Ptitsyn, and Lavrent'ev (89) have reported

$$\mathrm{Pt(SCN)_4^{-2}(aq) + 2SCN^-(aq) = Pt(SCN)_6^{-2}(aq) + 2e^-} \qquad E(1\ M\ \mathrm{NaSCN}) = -0.47\ \mathrm{v}$$

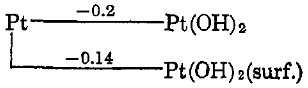
Chernyaev, Zemskov, and Ptitsyn (44) report the following.

SCHEME VI

ACIDIC OR NEUTRAL SOLUTION



BASIC SOLUTION



$$Pt(NO_2)_4^{-2}(aq) + 2Cl^-(aq) = Pt(NO_2)_4Cl_2^{-2}(aq) + 2e^- \quad E(0.05\ M\ KCl) = -0.65\ v$$

$$Pt(NO_2)_4^{-2}(aq) + 2NO_2^-(aq) = Pt(NO_2)_6^{-2}(aq) + 2e^- \quad E(0.028\ M\ KNO_2) = -0.34\ v$$

They (44) and Chernyaev, Muraveiskaya, and Korablina (39) report potentials for several mixed Pt(II)|Pt(IV) couples involving $NO_2^-(aq)$, $Br^-(aq)$, $Cl^-(aq)$, and $NH_3(aq)$.

Thermodynamic functions for ion pairing of $Pt(en)_3^{+4}(aq)$ with various anions have been determined (71, 140). Leden and Chatt (119) reported equilibrium quotients for reaction of $Pt(C_2H_4)Cl_3^-(aq)$ with several ligands. Equilibrium constants have been reported (53, 54, 55, 98) for association of $PtCl_4^{-2}(aq)$ with various olefins and alcohols containing ammine functions.

Many of the potentials discussed on preceding pages and the related stabilities of various oxidation states can be summarized by the potential diagrams in Scheme VI.

Before closing this discussion of the platinum group, we emphasize once again that there are very large uncertainties associated with many of the thermodynamic quantities we have tabulated. In some cases there may be errors in our tabulated quantities because we have made a wrong choice in which of several conflicting sets of experimental results to adopt. These problems can be settled only by further experimental work.

ACKNOWLEDGMENT.—We thank C. A. Wulff of the University of Vermont for his preliminary literature work, D. D. Wagman and W. H. Evans of the National Bureau of Standards for their helpful discussions, and Mrs. M. Garbuny for her generous help in translating many of the foreign-language articles. We also acknowledge financial support from the National Science Foundation.

VIII. REFERENCES

(1) Alcock, C. B., and Hooper, G. W., *Proc. Roy. Soc.* (London), **A254**, 551 (1960).
(2) Anderson, L. H., and Yost, D. M., *J. Am. Chem. Soc.*, **60**, 1822 (1938).
(3) Anson, F. C., *J. Chem. Educ.*, **36**, 394 (1959).
(4) Archibald, E. H., Wilcox, W. G., and Buckley, B. G., *J. Am. Chem. Soc.*, **30**, 747 (1908).
(5) Ariya, S. M., Morozova, M. P., and Reikhardt, A. A., *Zh. Obshch., Khim.*, **23**, 1455 (1953).
(6) Atwood, D. K., and De Vries, T., *J. Am. Chem. Soc.*, **84**, 2659 (1962).
(7) Babaeva, A. V., and Khananova, E. Y., *Zh. Neorg. Khim.*, **10**, 2579 (1965); *Russ. J. Inorg. Chem.*, **10**, 1402 (1965).
(8) Babeliowsky, T. P. J. H., *Physica*, **28**, 1160 (1962).
(9) Backhouse, J. R., and Dwyer, F. P., *J. Proc. Roy. Soc. N. S. Wales*, **83**, 138 (1949).
(10) Backhouse, J. R., and Dwyer, F. P., *J. Proc. Roy. Soc. N. S. Wales*, **83**, 146 (1949).
(11) Bartlett, N., and Rao, P. R., *Proc. Chem. Soc.*, 393 (1964).
(12) Basolo, F., and Pearson, R. G., *Progr. Inorg. Chem.*, **4**, 381 (1962).
(13) Bell, W. E., Garrison, M. C., and Merten, U., *J. Phys. Chem.*, **64**, 145 (1960).
(14) Bell, W. E., Garrison, M. C., and Merten, U., *J. Phys. Chem.*, **65**, 517 (1961).
(15) Bell, W. E., Inyard, R. E., and Tagami, M., *J. Phys. Chem.*, **70**, 3735 (1966).
(16) Bell, W. E., Merten, U., and Tagami, M., *J. Phys. Chem.*, **65**, 510 (1961).
(17) Bell, W. E., and Tagami, M., *J. Phys. Chem.*, **67**, 2432 (1963).
(18) Bell, W. E., and Tagami, M., *J. Phys. Chem.*, **70**, 640 (1966).
(19) Bell, W. E., and Tagami, M., *J. Phys. Chem.*, **70**, 3736 (1966).
(20) Bell, W. E., Tagami, M., and Inyard, R. E., *J. Phys. Chem.*, **70**, 2048 (1966).
(21) Bell, W. E., Tagami, M., and Merten, U., *J. Phys. Chem.*, **66**, 490 (1962).
(22) Biltz, W., and Juza, R., *Z. Anorg. Allgem. Chem.*, **190**, 161 (1930).
(23) Biltz, W., and Laar, J., *Z. Anorg. Allgem. Chem.*, **228**, 257 (1936).
(24) Biltz, W., Laar, J., Ehrlich, P., and Maisel, K., *Z. Anorg. Allgem. Chem.*, **233**, 257 (1937).
(25) Biryukov, A. A., and Shlenskaya, V. I., *Zh. Neorg. Khim.*, **9**, 813 (1964); *Russ. J. Inorg. Chem.*, **9**, 450 (1964).
(26) Biryukov, A. A., Shlenskaya, V. I., and Alimarin, I. P., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 3 (1966); *Chem. Abstr.*, **64**, 10740 (1966).
(27) Brewer, L., *Chem. Rev.*, **52**, 1 (1953).
(28) Broomhead, J. A., Basolo, F., and Pearson, R. G., *Inorg. Chem.*, **3**, 826 (1964).
(29) Buck, T. M., Jr., Wallace, W. E., and Rulon, R. M., *J. Am. Chem. Soc.*, **74**, 136 (1952).
(30) Buckingham, D. A., Dwyer, F. P., and Sargeson, A. M., *Inorg. Chem.*, **5**, 1243 (1966).
(31) Buckley, R. R., and Mercer, E. E., *J. Phys. Chem.*, **70**, 3103 (1966); Mercer, E. E., and Buckley, R. R., *Inorg. Chem.*, **4**, 1692 (1965).
(32) Burger, K., *Acta Chim. Acad. Sci. Hung.*, **40**, 261 (1964).
(33) Burger, K., and Dyrssen, D., *Acta Chem. Scand.*, **17**, 1489 (1963).
(34) Cady, G. H., and Hargreaves, G. B., *J. Chem. Soc.*, 1563 (1961).
(35) Cady, G. H., and Hargreaves, G. B., *J. Chem. Soc.*, 1568 (1961).
(36) Carrera, N. J., Walker, R. F., and Plante, E. R., *J. Res. Natl. Bur. Std.*, **68A**, 325 (1964).
(37) Cartledge, G. H., *J. Phys. Chem.*, **60**, 1468 (1956).
(38) Chang, J. C., and Garner, C. S., *Inorg. Chem.*, **4**, 209 (1965).
(39) Chernyaev, I. I., Muraveiskaya, G. S., and Korablina, L. S., *Zh. Neorg. Khim.*, 11, 1339 (1966); *Russ. J. Inorg. Chem.*, 11, 714 (1966).
(40) Chernyaev, I. I., and Palkin, V. A., *Izv. Sektora Platiny i Drug. Blagorodr. Metal., Inst. Obshch. i Neorg. Khim., Akad. Nauk SSSR*, **30**, 92 (1955); *Chem. Abstr.*, **50**, 9848 (1956).
(41) Chernyaev, I. I., and Palkin, V. A., *Zh. Neorg. Khim.*, 1, 890 (1956); *Russ. J. Inorg. Chem.*, 1 (5), 11 (1956).
(42) Chernyaev, I. I., Palkin, V. A., and Baranova, R. A., *Zh. Neorg. Khim.*, **5**, 821 (1960); *Russ. J. Inorg. Chem.*, **5**, 394 (1960).
(43) Chernyaev, I. I., Palkin, V. A., Baranova, R. A., and Kuz'mina, N. N., *Zh. Neorg. Khim.*, **5**, 1428 (1960); *Russ. J. Inorg. Chem.*, **5**, 693 (1960).

(44) Chernyaev, I. I., Zemskov, S. V., and Ptitsyn, B. V., *Zh. Neorg. Khim.*, **10**, 2404 (1965); *Russ. J. Inorg. Chem.*, **10**, 1309 (1965).

(45) Connick, R. E., and Hurley, C. R., *J. Am. Chem. Soc.*, **74**, 5012 (1952).

(46) Connick, R. E., and Hurley, C. R., *J. Phys. Chem.*, **61**, 1018 (1957).

(47) Cordfunke, E. H. P., and Meyer, G., *Rec. Trav. Chim.*, **81**, 495, 670 (1962).

(48) Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1966.

(49) Coulter, L. V., Pitzer, K. S., and Latimer, W. M., *J. Am. Chem. Soc.*, **62**, 2845 (1940).

(50) Cozzi, D., and Pantani, F., *J. Inorg. Nucl. Chem.*, **8**, 385 (1958).

(51) deBethune, A. J., *J. Electrochem. Soc.*, **102**, 288c (1955).

(52) DeFord, D. D., and Davidson, A. W., *J. Am. Chem. Soc.*, **73**, 1469 (1951).

(53) Denning, R. G., Hartley, F. R., and Venanzi, L. M., *J. Chem. Soc.*, 324 (1967).

(54) Denning, R. G., Hartley, F. R., and Venanzi, L. M., *J. Chem. Soc.*, 328 (1967).

(55) Denning, R. G., and Venanzi, L. M., *J. Chem. Soc.*, 336 (1967).

(56) Dillard, J. G., and Kiser, R. W., *J. Phys. Chem.*, **69**, 3893 (1965).

(57) Dreger, L. H., and Margrave, J. L., *J. Phys. Chem.*, **64**, 1323 (1960).

(58) Dreger, L. H., and Margrave, J. L., *J. Phys. Chem.*, **65**, 2106 (1961).

(59) Droll, H. A., Block, B. P., and Fernelius, W. C., *J. Phys. Chem.*, **61**, 1000 (1957).

(60) Dunning, W. W., and Martin, D. S., Jr., *J. Am. Chem. Soc.*, **81**, 5566 (1959).

(61) Dwyer, F. P., Humpoletz, J. E., and Nyholm, R. S., *Proc. Roy. Soc. N. S. Wales*, **80**, 242 (1947).

(62) Dwyer, F. P., McKenzie, H. A., and Nyholm, R. S., *J. Proc. Roy. Soc. N. S. Wales*, **80**, 183 (1947).

(63) Dwyer, F. P., McKenzie, H. A., and Nyholm, R. S., *J. Proc. Roy. Soc. N. S. Wales*, **81**, 216 (1947).

(64) Dwyer, F. P., and Schafer, H. N., *J. Proc. Roy. Soc. N. S. Wales*, **82**, 294 (1948).

(65) El-Awady, A. A., Bounsall, E. J., and Garner, C. S., *Inorg. Chem.*, **6**, 79 (1967).

(66) Elding, L. I., and Leden, I., *Acta Chem. Scand.*, **20**, 706 (1966).

(67) Endicott, J. F., and Taube, H., *Inorg. Chem.*, **4**, 437 (1965).

(68) Fasman, A. B., Kutyukov, G. G., and Sokol'skii, D. V., *Zh. Neorg. Khim.*, **10**, 1338 (1965); *Russ. J. Inorg. Chem.*, **10**, 727 (1965).

(69) Forrester, J. S., and Ayres, G. H., *J. Phys. Chem.*, **63**, 1979 (1959).

(70) George, P., Hanania, G. I. H., and Irvine, D. H., *J. Chem. Soc.*, 3048 (1957).

(71) Giedt, D. C., and Nyman, C. J., *J. Phys. Chem.*, **67**, 2491 (1963).

(72) Gire, G., *Ann. Chim.*, **4**, 183 (1925).

(73) Gire, G., *Ann. Chim.*, **4**, 370 (1925).

(74) Gire, G., and Puche, F., *Compt. Rend.*, **200**, 670 (1935).

(75) Glemser, O., Roesky, H. W., Hellberg, K. H., and Werther, H. U., *Chem. Ber.*, **99**, 2652 (1966).

(76) Goldberg, R. N., Riddell, R. G., Wingard, M. R., Hopkins, H. P., Wulff, C. A., and Hepler, L. G., *J. Phys. Chem.*, **70**, 706 (1966).

(77) Golub, A. M., and Pomerants, G. B., *Zh. Neorg. Khim.*, **9**, 1624 (1964); *Russ. J. Inorg. Chem.*, **9**, 879 (1964).

(78) Gortsema, F. P., and Cobble, J. W., *J. Am. Chem. Soc.*, **83**, 4317 (1961).

(79) Griffith, W. P., *Quart. Rev.* (London), XIX, 254 (1965).

(80) Grinberg, A. A., and Gel'fman, M. I., *Dokl. Akad. Nauk SSSR*, **133**, 1081 (1960).

(81) Grinberg, A. A., and Gel'fman, M. I., *Dokl. Akad. Nauk SSSR*, **137**, 87 (1961).

(82) Grinberg, A. A., and Gel'fman, M. I., *Dokl. Akad. Nauk SSSR*, **149**, 1328 (1963).

(83) Grinberg, A. A., and Gel'fman, M. I., *Dokl. Akad. Nauk SSSR*, **150**, 305 (1963).

(84) Grinberg, A. A., Kiseleva, N. V., and Gel'fman, M. I., *Dokl. Akad. Nauk. SSSR*, **153**, 1327 (1963).

(85) Grinberg, A. A., Kiseleva, N. V., and Gel'fman, M. I., *Dokl. Akad. Nauk SSSR*, **172**, 856 (1967); *Chem. Abstr.*, **67**, 80064 (1967).

(86) Grinberg, A. A., and Lavrent'ev, V. N., *Compt. Rend. Acad. Sci. URSS*, **35**, 203 (1942).

(87) Grinberg, A. A., Lavrent'ev, V. N., and Ptitsyn, B. V., *Compt. Rend. Acad. Sci. URSS*, **26**, 52 (1940).

(88) Grinberg, A. A., and Orlova, B. Z., *Zh. Prikl. Khim.*, **22**, 441 (1949).

(89) Grinberg, A. A., Ptitsyn, B. V., and Lavrent'ev, V. N., *Zh. Fiz. Khim.*, **10**, 661 (1937).

(90) Grinberg, A. A., and Shagisultanova, G. A., *Zh. Neorg. Khim.*, **5**, 280 (1960); *Russ. J. Inorg. Chem.*, **5**, 134 (1960).

(91) Grinberg, A. A., and Shamsiev, A. S., *Zh. Obsch. Khim.*, **12**, 55 (1942).

(92) Grønvold, F., Thurmann-Moe, T., Westrum, E. F., Jr., and Chang, E., *J. Chem. Phys.*, **35**, 1665 (1961).

(93) Grube, G., and Autenrieth, H., *Z. Electrochem.*, **44**, 296 (1938).

(94) Grube, G., and Fromm, G., *Z. Electrochem.*, **47**, 208 (1941).

(95) Grube, G., and Gu, B., *Z. Electrochem.*, **43**, 397 (1937).

(96) Hampson, R. F., and Walker, R. F., *J. Res. Natl. Bur. Std.*, **65A**, 289 (1961).

(97) Hampson, R. F., and Walker, R. F., *J. Res. Natl. Bur. Std.*, **66A**, 177 (1962).

(98) Hartley, F. R., and Venanzi, L. M., *J. Chem. Soc.*, 330 (1967).

(99) Henry, P. M., *J. Am. Chem. Soc.*, **86**, 3246 (1964).

(99a) Hepler, L. G., and Gedanksy, L. M., to be published.

(100) Hoare, J. P., *J. Electrochem. Soc.*, 111, 232 (1964).

(101) Hoare, J. P., *J. Electrochem. Soc.*, 111, 988 (1964).

(102) Holloway, J. H., and Peacock, R. D., *J. Chem. Soc.*, 527 (1963).

(103) Isambert, *Compt. Rend.*, **91**, 768 (1880).

(104) Izatt, R. M., Eatough, D., and Christensen, J. J., *J. Chem. Soc.*, 1301 (1967).

(105) Izatt, R. M., Watt, G. D., Eatough, D., and Christensen, J. J., *J. Chem. Soc.*, 1304 (1967).

(105a) Jirsa, F., *Z. Physik. Chem.*, **113**, 241 (1924).

(106) Joannis, *Compt. Rend.*, **95**, 295 (1882).

(107) Jolly, W. L., *J. Chem. Educ.*, **43**, 198 (1966).

(108) Jusz, R., *Z. Anorg. Allgem. Chem.*, **219**, 129 (1934).

(109) Juza, R., and Meyer, W., *Z. Anorg. Allgem. Chem.*, **213**, 273 (1933).

(110) Kelley, K. K., U. S. Bureau of Mines Bulletin No. 383, U. S. Government Printing Office, Washington, D. C., 1935; reprinted as Bureau of Mines Bulletin No. 601, 1962.

(111) Kelley, K. K., U. S. Bureau of Mines Bulletin No. 584, U. S. Government Printing Office, Washington, D. C., 1960.

(112) Kelley, K. K., and King, E. G., U. S. Bureau of Mines

Bulletin No. 592, U. S. Government Printing Office, Washington, D. C., 1961.

(113) Kolbin, N. I., Samoilov, V. M., and Ryabov, A. N., *Khim. Redkikh Elementov, Leningr. Gos. Univ.*, 50 (1964); *Chem. Abstr.*, **61**, 10106 (1964).

(114) Kolbin, N. I., and Semenov, I. N., *Zh. Neorg. Khim.*, **9**, 203 (1964); *Russ. J. Inorg. Chem.*, **9**, 108 (1964).

(115) Kolbin, N. I., Semenov, I. N., and Shutov, Yu. M., *Zh. Neorg. Khim.*, **9**, 1029 (1964); *Russ. J. Inorg. Chem.*, **9**, 563 (1964).

(116) Kravtsov, V. I., and Petrova, G. M., *Zh. Neorg. Khim.*, **9**, 1010 (1964); *Russ. J. Inorg. Chem.*, **9**, 552 (1964).

(117) Kravtsov, V. I., and Zelenskii, M. I., *Elektrokhimiya*, **2**, 1138 (1966); *Chem. Abstr.*, **66**, 34182 (1967).

(118) Latimer, W. M., "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952.

(119) Leden, I., and Chatt, J., *J. Chem. Soc.*, 2936 (1955).

(120) Lewis, G. N., and Randall, M. (revised by K. S. Pitzer and L. Brewer), "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1961.

(121) Licht, T. S., and deBethune, A. J., *J. Chem. Educ.*, **34**, 433 (1957).

(122) Lippincott, E. R., and Nelson, R. D., *J. Am. Chem. Soc.*, **77**, 4990 (1955).

(123) Luoma, E. V., and Brubaker, C. H., Jr., *Inorg. Chem.*, **5**, 1637 (1966).

(124) Martin, F. S., *J. Chem. Soc.*, 2564 (1954).

(125) Mason, W. R., III, Berger, E. R., and Johnson, R. C., *Inorg. Chem.*, **6**, 248 (1967).

(126) Mercer, E. E., Campbell, W. M., Jr., and Wallace, R. M., *Inorg. Chem.*, **3**, 1018 (1964).

(127) Mertes, R. W., Crowell, W. R., and Brinton, R. K., *J. Am. Chem. Soc.*, **72**, 4218 (1950).

(128) Miller, V. F., and Terrey, H., *J. Chem. Soc.*, 605 (1927).

(129) Murmann, R. K., and Sullivan, J. C., *Inorg. Chem.*, **6**, 892 (1967).

(130) Nace, D. M., and Aston, J. G., *J. Am. Chem. Soc.*, **79**, 3619 (1957).

(131) Nagarajan, G., *Bull. Soc. Chim. Belges*, **71**, 77 (1962).

(132) Nagarajan, G., *Indian J. Pure Appl. Phys.*, **2**, 86 (1964).

(133) Nikol'skii, A. B., *Zh. Neorg. Khim.*, **8**, 1045 (1963); *Russ. J. Inorg. Chem.*, **8**, 541 (1963); *Zh. Neorg. Khim.*, **10**, 290 (1965); *Russ. J. Inorg. Chem.*, **10**, 152 (1965).

(134) Nikol'skii, A. B., *Zh. Neorg. Khim.*, **9**, 2511 (1964); *Russ. J. Inorg. Chem.*, **9**, 1356 (1964).

(135) Nikol'skii, A. B., and Ryabov, A. N., *Zh. Neorg. Khim.*, **9**, 7 (1964); *Russ. J. Inorg. Chem.*, **9**, 3 (1964).

(136) Nikol'skii, A. B., Semenov, G. A., and Veshnyakova, E. N., *Zh. Neorg. Khim.*, **12**, 1087 (1967); *Chem. Abstr.*, **67**, 26185 (1967).

(137) Niwa, K., Yokokawa, T., and Isoya, T., *Bull. Chem. Soc. Japan*, **35**, 1543 (1962).

(138) Norman, J. H., Staley, H. G., and Bell, W. E., *J. Phys. Chem.*, **69**, 1373 (1965).

(139) Novak, B., and Markovic, T., *Monatsh. Chem.*, **94**, 607 (1963).

(140) Nyman, C. J., and Plane, R. A., *J. Am. Chem. Soc.*, **82**, 5787 (1960).

(141) Oranskaya, M. A., and Mikhailova, N. A., *Zh. Neorg. Khim.*, **5**, 12 (1961); *Russ. J. Inorg. Chem.*, **5**, 5 (1961).

(142) Ortner, M. H., *J. Chem. Phys.*, **34**, 556 (1961).

(143) Palkin, V. A., Kuz'mina, N. N., and Chernyaev, I. I., *Zh. Neorg. Khim.*, **10**, 1792 (1965); *Russ. J. Inorg. Chem.*, **10**, 978 (1965).

(144) Panish, M. B., and Reif, L., *J. Chem. Phys.*, **34**, 1915 (1961).

(145) Panish, M. B.. and Reif, L., *J. Chem. Phys.*, **37**, 128 (1962).

(146) Paule, R. C., and Margrave, J. L., *J. Phys. Chem.*, **67**, 1896 (1963).

(147) Pigeon, L., *Ann. Chim. Phys.*, **2**, 433 (1894).

(148) Plumb, W., and Harris, G. M., *Inorg. Chem.*, **3**, 542 (1964).

(149) Poë, A. J., and Vaidya, M. S., *J. Chem. Soc.*, 3431 (1960).

(150) Popovicheva, N. K., Biryukov, A. A., and Shlenskaya, V. I., *Zh. Neorg. Khim.*, **9**, 1482 (1964); *Russ. J. Inorg. Chem.*, **9**, 803 (1964).

(151) Porte, H. A., Greenbeerg, E., and Hubbard, W. N., *J. Phys. Chem.*, **69**, 2308 (1965).

(152) Ptitsyn, B. V., *Zh. Obshch. Khim.*, **15**, 277 (1945); *Chem. Abstr.*, **40**, 3357 (1946).

(153) Puche, F., *Ann. Chim.*, **9**, 233 (1938).

(154) Ramsay, J. B., *J. Electrochem. Soc.*, **104**, 255, 691 (1957); *J. Chem. Educ.* **38**, 353 (1961).

(155) Reinhardt, R. A., *Inorg. Chem.*, **1**, 839 (1962).

(156) Reinhardt, R. A., Brenner, N. L., and Sparkes, R. K., *Inorg. Chem.*, **6**, 254 (1967).

(157) Remy, H., *Z. Anorg. Allgem. Chem.*, **137**, 365 (1924).

(158) Remy, H., *Z. Angew. Chem.*, **39**, 1061 (1926).

(159) Rettew, R. R., and Johnson, R. C., *Inorg. Chem.*, **4**, 1565 (1965).

(160) Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, I., "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(161) Sanders, C. I., and Martin, D. S., Jr., *J. Am. Chem. Soc.*, **83**, 807 (1961).

(162) Sauerbrunn, R. D., and Sandell, E. B., *J. Am. Chem. Soc.*, **75**, 4170 (1953).

(163) Sawyer, D. T., and Interrante, L. V., *J. Electroanal. Chem.*, **2**, 310 (1961).

(164) Schäfer, H., and Heitland, H. J., *Z. Anorg. Allgem. Chem.*, **304**, 249 (1960).

(165) Schäfer, H., Schneidereit, G., and Gerhardt, W., *Z. Anorg. Allgem. Chem.*, **319**, 327 (1963).

(166) Schäfer, H., and Tebben, A., *Z. Anorg. Allgem. Chem.*, **304**, 317 (1960).

(167) Schäfer, H., Tebben, A., and Gerhardt, W., *Z. Anorg. Allgem. Chem.*, **321**, 41 (1963).

(168) Schmahl, N. G., and Minzl, E., *Z. Physik. Chem.* (Frankfurt), **41**, 78 (1964).

(169) Schmahl, N. G., and Minzl, E., *Z. Physik. Chem.* (Frankfurt), **47**, 142 (1965).

(170) Scrivastava, S. S., and Newman, L., *Inorg. Chem.*, **5**, 1506 (1966).

(171) Shchukarev, S. A., Kolbin, N. I., and Ryabov, A. N., *Zh. Neorg. Khim.*, **3**, 1721 (1958); *Russ. J. Inorg. Chem.*, **3** (8), 1 (1958).

(172) Shchukarev, S. A., Kolbin, N. I., and Ryabov, A. N., *Vestn. Leningr. Univ., Ser. Fiz. i Khim.*, **16**, 100 (1961); *Chem. Abstr.*, **55**, 15200 (1961).

(173) Shchukarev, S. A., Kolbin, N. I., and Ryabov, A. N., *Zh. Neorg. Khim.*, **6**, 1013 (1961); *Russ. J. Inorg. Chem.*, **6**, 517 (1961).

(174) Shchukarev, S. A., Lobaneva, O. A., Ivanova, M. A., and Kononova, M. A., *Vestn. Leningr. Univ., Ser. Fiz. i Khim.*, **16**, 152 (1961); *Chem. Abstr.*, **55**, 24362 (1961).

(175) Shchukarev, S. A., Lobaneva, O. A., Ivanova, M. A., and Kononova, M. A., *Zh. Neorg. Khim.*, **9**, 2791 (1964); *Russ. J. Inorg. Chem.*, **9**, 1503 (1964).

(176) Shchukarev, S. A., Oranskaya, M. A., and Shemyakina, T. S., *Zh. Neorg. Khim.*, **1**, 17 (1956); *Russ. J. Inorg. Chem.*, **1**, 17 (1956).

(177) Shchukarev, S. A., and Ryabov, A. N., *Zh. Neorg. Khim.*, **5**, 1931 (1960); *Russ. J. Inorg. Chem.*, **5**, 941 (1960).

(178) Shchukarev, S. A., Tolmacheva, T. A., Oranskaya, M. A., and Komandrovskaya, L. V., *Zh. Neorg. Khim.*, 1, 8 (1956); *Russ. J. Inorg. Chem.*, 1, 7 (1956).

(179) Shchukarev, S. A., Tolmacheva, T. A., and Pazukhina, Yu. L., *Zh. Neorg. Khim.*, **9**, 2507 (1964); *Russ. J. Inorg. Chem.*, **9**, 1354 (1964).

(180) Shchukarev, S. A., Tolmacheva, T. A., and Slavutskaya, G. M., *Zh. Neorg. Khim.*, **9**, 2501 (1964); *Russ. J. Inorg. Chem.*, **9**, 1351 (1964).

(181) Sherif, F. G., and Michail, K. F., *J. Inorg. Nucl. Chem.*, **25**, 999 (1963).

(182) Shidlovskii, A. A., and Valkina, K. V., *Zh. Fiz. Khim.*, **35**, 294 (1961).

(183) Shlenskaya, V. I., and Biryukov, A. A., *Zh. Neorg. Khim.*, 11, 54 (1966); *Russ. J. Inorg. Chem.*, 11, 28 (1966).

(184) Shlenskaya, V. I., Biryukov, A. A., and Moskovkina, E. M., *Zh. Neorg. Khim.*, 11, 600 (1966); *Russ. J. Inorg. Chem.*, 11, 325 (1966).

(185) Shlenskaya, V. I., Khvostova, V. P., and Peshkova, V. M., *Zh. Anal. Khim.*, **17**, 598 (1962).

(186) Shukla, S. K., *Ann. Chim.* (Paris), **6**, 1383 (1961).

(187) Silverman, M. D., and Levy, H. A., *J. Am. Chem. Soc.*, **76**, 3319 (1954).

(188) Smith, E. R., *J. Res. Natl. Bur. Std.*, **5**, 735 (1930).

(189) Subbotina, N. A., Zheligovskaya, N. N., and Pashinkin, A. S., *Zh. Neorg. Khim.*, 11, 2393 (1966); *Russ. J. Inorg. Chem.*, 11, 1283 (1966).

(190) Sundaram, S., *Z. Physik. Chem.* (Frankfurt), **34**, 225 (1962).

(191) Templeton, D. H., Watt, G. W., and Garner, C. S., *J. Am. Chem. Soc.*, **65**, 1608 (1943).

(192) Terrey, H., *J. Chem. Soc.*, 202 (1928).

(193) Thomsen, J., "Thermochemistry," Longmans, Green and Co., London, 1908.

(194) Trulson, O. C., and Schissel, P. O., NASA Accession No. N65-11997, Rept. No. AD 449865; *Chem. Abstr.*, **63**, 74 (1965).

(195) von Wartenberg, H., *Ann.*, **440**, 97 (1924).

(196) Wagman, D. D., Evans, W. H., Halow, I., Parker, V. B., Bailey, S. M., and Schumm, R. H., National Bureau of Standards Technical Note 270-1, U. S. Government Printing Office, Washington, D. C., 1965.

(197) Wallace, R. M., *J. Phys. Chem.*, **68**, 2418 (1964).

(198) Walsh, T. J., and Hausman, E. A., in "Treatise on Analytical Chemistry," Vol. 8, I. M. Kolthoff, P. J. Elving, and E. B. Sandell, Ed., Interscience Publishers, Inc., New York, N. Y., 1963.

(199) Warner, J. S., *J. Electrochem. Soc.*, **114**, 68 (1967).

(200) Weed, E. D., Ph.D. Thesis, The Ohio State University, 1964; *Dissertation Abstr.*, **25**, 795 (1964).

(201) Wehner, P., and Hindman, J. C., *J. Am. Chem. Soc.*, **72**, 3911 (1950).

(202) Weinstock, B., Claassen, H. H., and Malm, J. G., *J. Chem. Phys.*, **32**, 181 (1960).

(203) Weinstock, B., Malm, J. G., and Weaver, E. E., *J. Am. Chem. Soc.*, **83**, 4310 (1961).

(204) Wellman, H. B., *J. Am. Chem. Soc.*, **52**, 985 (1930).

(205) Westrum, E. F., Jr., Carlson, H. G., Grønvold, F., and Kjekshus, A., *J. Chem. Phys.*, **35**, 1670 (1961).

(206) Willis, J. B., *J. Am. Chem. Soc.*, **66**, 1067 (1944).

(207) Wöhler, L., and Jochum, N., *Z. Physik. Chem.*, **A167**, 169 (1933).

(208) Wöhler, L., and Müller, W., *Z. Anorg. Allgem. Chem.*, **149**, 125 (1925).

(209) Wöhler, L., and Streicher, S., *Ber.*, **46**, 1577 (1913).

(210) Yamamoto, H., and Takei, T., *J. Electrochem. Soc. Japan*, **29**, E119 (1961).

(211) Yamamoto, H., Tanaka, S., Nagai, T., and Takei, T., *Denki Kagaku*, **32**, 43 (1964); *Chem. Abstr.*, **61**, 10317 (1964).

(212) Zavitsanos, P. D., *J. Phys. Chem.*, **68**, 2899 (1964).